

INSTITUTE OF LOW TEMPERATURE AND
STRUCTURE RESEARCH

POLISH ACADEMY OF SCIENCE



DOCTORAL DISSERTATION

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Synthesis and optical properties of carbon dots and their application in photodegradation of organic compounds and sensing

in the form of a thematically coherent series of articles published and prepared for
submission

Supervisor: Ph. D. Paweł Głuchowski

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*I would like to express my deepest and most heartfelt gratitude
to my fiancé, Edgar, my mum, my dad and my sister, Lena.*

*Your support, faith in me, and motivation through difficult times,
as well as celebrating my success together are my most precious memories.*

*I dedicate this thesis to you, because without you, it would not exist.
Thank you for standing by me in the valleys and sharing my joy on the highest peaks.*

*I would also like to express my sincere gratitude to
my supervisor dr. hab. **Paweł Gluchowski, prof. INTiBS PAN.**
The years of our collaboration have been incredibly educational for me – thanks to
them, I have not only become a better scientist but also grown as a person.*

*I would like to thank **my colleagues** for the fruitful
collaboration that resulted in such fascinating research.*

*I extend special gratitude to **Agata and Ola,**
who always knew when things weren't going my way*

*And finally, I would like to congratulate myself.
The amount of work, sacrifice, and energy this journey required fills me with pride.
Despite numerous hardships, hostility, and obstacles thrown in my path to
throw me off course, today I stand proudly with a huge smile in this place. :D*

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1. Abstract

This doctoral dissertation is devoted to the design, synthesis, and characterization of the optical properties of carbon dots (CDs) for applications in molecular sensing and heterogeneous photocatalysis. The main aim of this thesis was to explain the correlation between surface chemistry and luminescence mechanisms, which is an important factor in tuning the functionality of carbon dots, and to apply this knowledge to the design of photocatalytic hybrid materials.

The research was conducted in four distinct stages. In the first stage, detailed studies were carried out on the influence of acidic, alkaline and aprotic chemical modifiers on the spectroscopic parameters of CDs. It was demonstrated that the selection of the synthesis environment allows for precise control over emission mechanisms, ranging from the stabilization of surface trap states (STS) in an acidic environment, which extends fluorescence lifetimes, to charge transfer (CT) processes in an alkaline and aprotic environment, enabling high quantum yield (QY) of up to 80%.

The second stage of the work examined the effect of environmental conditions on the optical properties of CDs. The resulting nanostructures exhibited a linear spectral response over a broad pH range (1-14) and a high sensitivity to the presence of hydroxyl groups in organic solvents. Using advanced spectroscopic diagnostics- including Fourier-Transform Infrared Spectroscopy (FTIR), alongside excitation and emission profiling - it was demonstrated that the sensing mechanism relies on dynamic surface interactions and structural transformations at the material-analyte interface.

The third part of the dissertation examined the potential of CDs as components of hybrid photocatalytic systems. By integrating fluorescent and phosphorescent CDs with mesoporous TiO₂, materials with enhanced activity for the photodegradation of carbamazepine (CBZ) were obtained with the possibility of using visible light in this process. The results confirmed that CDs play a triple role in these systems: extending the absorption range of the matrix, acting as electron acceptors that suppress charge carrier recombination, and serving as active centers that increase the efficiency of electron-hole pair separation.

The fourth part examined how interfacial engineering strategies and the structural reorganization of the interface between CDs and ZnO allow for the precise modulation of the hybrid's catalytic properties. By developing and systematically analyzing five distinct modification paths it was demonstrated that the architecture of the heterojunction determines whether oxidative or reductive photocatalytic pathways are selectively promoted under UV-Vis light. The results revealed that while the presence of the organic phase can introduce competitive consumption of reactive oxygen species (ROS) due to autophotodegradation, specific approaches to hybrid materials preparation such as hydrothermal processing enhance charge transfer and result in exhaustive degradation of reaction intermediates like naproxen (NPX).

In summary, the results presented in this thesis demonstrate that CDs are materials with properties that can be precisely tuned through surface chemistry modification. The research conducted expands knowledge of photophysical processes in carbon nanostructures and indicates new possibilities for their application in modern environmental remediation technologies and advanced chemical analytics.

2. Streszczenie

Niniejsza rozprawa doktorska poświęcona jest projektowaniu, syntezie oraz charakterystyce właściwości optycznych kropek węglowych (CDs) do zastosowań jako czujniki molekularne i w fotokatalizie heterogenicznej. Głównym celem niniejszej rozprawy było wyjaśnienie korelacji pomiędzy chemią powierzchni a mechanizmami luminescencji, co stanowi ważny czynnik w dostrajaniu funkcjonalności kropek węglowych, oraz zastosowanie tej wiedzy w projektowaniu fotokatalitycznych materiałów hybrydowych.

W ramach przeprowadzonych badań zrealizowano cztery główne etapy badawcze. W pierwszym etapie przeprowadzono szczegółowe badania dotyczące wpływu kwasowych, zasadowych i aprotycznych modyfikatorów chemicznych na właściwości optyczne CDs. Wykazano, że dobór środowiska syntezy pozwala na precyzyjną kontrolę mechanizmów emisji – od stabilizacji powierzchniowych stanów pułpkowych w środowisku kwasowym, prowadzącej do wydłużenia czasów życia fluorescencji, po procesy transferu ładunku w środowisku zasadowym i aprotycznym, umożliwiające osiągnięcie wysokiej wydajności kwantowej dochodzącej do 80%.

Drugi etap prac dotyczył zbadania wpływu warunków środowiskowych na właściwości optyczne CDs. Otrzymane nanostruktury wykazały zdolność do liniowej odpowiedzi spektralnej w szerokim zakresie pH (1-14) oraz wysoką czułość na obecność grup hydroksylowych w rozpuszczalnikach organicznych. Za pomocą różnych technik spektroskopowych (FTIR, wzbudzenie, emisja) udowodniono, że mechanizm odpowiedzi opiera się na dynamicznych oddziaływaniach powierzchniowych oraz transformacjach strukturalnych zachodzących na granicy faz kropka–analit.

W trzeciej części pracy zbadano potencjał CDs jako komponentów hybrydowych układów fotokatalitycznych. Poprzez integrację fluorescencyjnych i fosforescencyjnych CDs z mezoporowatym TiO_2 , otrzymano materiały o podwyższonej aktywności w procesie degradacji karbamazepiny oraz możliwość wykorzystania światła widzialnego do przeprowadzenia tego procesu. Wyniki potwierdziły, że CDs pełnią w tych układach potrójną rolę: rozszerzają zakres absorpcji hybrydy, przejmują elektrony spowalniając

rekombinację nośników ładunku oraz są centrami aktywnymi zwiększającymi wydajność separacji par elektron-dziura.

W czwartej części zbadano, w jaki sposób strategie inżynierii międzyfazowej oraz strukturalna reorganizacja interfejsów między CDs a ZnO pozwalają na precyzyjną modulację właściwości katalitycznych otrzymanych materiałów hybrydowych. Poprzez opracowanie i analizę pięciu odrębnych ścieżek modyfikacji wykazano, że architektura wytworzonego heterozłącza determinuje selektywne promowanie oksydacyjnych bądź redukcyjnych procesów fotokatalitycznych w świetle UV-Vis. Wyniki ujawniły, że chociaż obecność fazy organicznej może prowadzić do konkurencyjnego zużycia ROS w wyniku autofotodegradacji fazy węglowej, to zastosowanie odpowiednich metod otrzymywania materiałów hybrydowych takich jak obróbka hydrotermalna, usprawnia transfer ładunku, umożliwiając głęboki rozkład produktów pośrednich oraz skuteczną degradację naproksenu (NPX).

Podsumowując, wyniki przedstawione w rozprawie dowodzą, że kropki węglowe są materiałami, których właściwości mogą być precyzyjnie dostrajane poprzez modyfikację powierzchni grupami funkcyjnymi. Przeprowadzone badania poszerzają wiedzę na temat procesów fotofizycznych zachodzących w nanostrukturach węglowych i pokazuje nowe możliwości ich wykorzystania w nowoczesnych technologiach oczyszczania środowiska oraz zaawansowanej analityce chemicznej.

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EDUCATION

2016-2020 **Engineer studies**, Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, Poland

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Investigator – NCBR LIDER 26/0121/L-2/20/NCBR/2021 “Biodegradable, selective, optical markers for securing goods and their detection system” (2021-2024)

Investigator – NCN OPUS 2021/41/B/ST5/01684 “Ferroelectric and nonlinear optical properties of hybrid organic-inorganic coordination polymers triggered by halogenation of ammonium cations” (2024)

Investigator – NCN SONATA 2023/51/D/ST5/00193 “Low-phonon nanocrystals doped with lanthanide ions – new materials for efficient up-conversion and photon avalanche” (2025-2026)

Investigator – NCN SONATA 2023/51/D/ST11/00475 “Understanding Up-conversion Resonant Energy Transfer to pH-Sensitive Fluorescent Dyes: From Novel Core-Shell

Luminescent Nanomaterials to Sensitive, Background-Free, and Broad-Range pH Sensing” (2025-2026)

PUBLICATIONS INCLUDED IN THE DOCTORAL DISSERTATION

P1. D.Kujawa, R. Tomala, P. Gluchowski, *Tailoring Emission Mechanisms in Carbon Dots through Controlled Surface Chemistry*, Applied Surface Science, 2026, 736, 10.1016/j.apsusc.2026.166772, (IF = 6.9, MNiSW Points: 140)

P2. D.Kujawa, M. Ptak, P. Gluchowski, *A Rapid, Green and Cost-Effective Synthesis of pH- and Hydroxyl Group Sensitive Carbon Dots for Sensing Applications*, Journal of Materials Chemistry C, 2025, 13, 32, 16364-72, 10.1039/D5TC02262B, (IF = 5.2, MNiSW Points: 140)

P3. D. Kujawa, A. Grzegorska, A. Zielinska-Jurek, M. Fandzloch, O. Bezkrvnyi, P. Gluchowski, *Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst*, Dalton Transactions, 2025, 54(4), 1504-1520, 10.1039/D4DT02196G, (IF = 3.3, MNiSW Points: 140)

P4. D. Kujawa, M. Kowalkińska, O. Bezkrvnyi, A. Zielińska-Jurek, P. Głuchowski. *CDs@ZnO Photocatalysts with Interfacial-Dependent Oxidative and Reductive Activity*, - manuscript ready for submission

PUBLICATIONS BEYOND THE SCOPE OF THE DOCTORAL DISSERTATION

P5. P. Głuchowski, **D. Kujawa**, D. Czekanowska, Q. Chen, A. Musiałek, K. Szustakiewicz, I. Smolina, T. Wu, M. Starykevich, C. Blawert, M. Serdechnova, *Exploring Er_{0.02}Yb_{0.4}Y_{1.58}O₃ powder additives producing multifunctional coatings on magnesium alloy via the PEO technique*, Applied Surface Science, 2025, 712, 10.1016/j.apsusc.2025.164241, (IF = 6.9, MNiSW Points: 140)

P6. M. Godzierz, O. Masiuchok, V. Talaniuk, K. Kurtyka, K. Olszowska, A. Kobyliukh, H. Janeczek, S. Pusz, P. Głuchowski, **D. Kujawa**, B. Toroń, P. Szperlich, P. Olesik, J. Smoleń, M. Kozioł, U. Szeluga, *Design of piezoelectric nanogenerator based on BiFeO₃/epoxy resin with potential application for wearable electronic devices*, Journal of

Applied Polymer Science, 2024, 141(6), 10.1002/app.54932, (IF = 2.8, MNiSW Points: 70)

P7. M. Chaika, **D. Kujawa**, W. Strek, P. Gluchowski, *Exploring the Impact of Nanorod Diameter on Near Infrared Laser-Induced Stokes and Anti-Stokes Emission in $La_{1-x}Nd_xAlO_3$* , The Journal of Physical Chemistry C, 2024, 128(19), 7999-8006, 10.1021/acs.jpcc.4c01657, (IF = 3.3, MNiSW Points: 140)

P8. P. Gluchowski, R. Nikonkov, **D. Kujawa**, W. Strek, T. Murauskas, A. Pakalniskis, A. Kareiva, A. Yaremkevych, O. Fesenko, A. Zhaludkevich, D. Karpinsky, *Controlling the Magnetic Properties of $La_{0.9}A_{0.1}Mn_{0.9}Cr_{0.1}O_3$ (A: Li, K, Na) Powders and Ceramics by Alkali Ions Doping*, Magnetochemistry, 2023, 9(6), 10.3390/magnetochemistry9060140, (IF = 2.5, MNiSW Points: 20)

P9. **D. Kujawa**, D. Szewczyk, V. Boiko, D. Beben, P. Gluchowski, *Effect of graphene addition on the thermal and persistent luminescence properties of $Gd_{2.994}Ce_{0.006}Ga_3Al_2O_{12}$ and $Gd_{2.964}Ce_{0.006}Dy_{0.03}Ga_3Al_2O_{12}$ ceramics*, Materials, 2022, 15(7), 10.3390/ma15072606, (IF = 3.2, MNiSW Points: 140)

P10. P. Gluchowski, R. Tomala, **D. Kujawa**, V. Boiko, T. Murauskas, P. Solarz, *Insights into the Relationship between Crystallite Size, Sintering Pressure, Temperature Sensitivity, and Persistent Luminescence Color of $Gd_{2.97}Pr_{0.03}Ga_3Al_2O_{12}$ Powders and Ceramics*, The Journal of Physical Chemistry C, 2022, 126(6), 7127-7142, 10.1021/acs.jpcc.2c00672, (IF = 3.3, MNiSW Points: 140)

P11. M. Rygala, K. Ryczko, T. Smolka, **D. Kujawa**, P. Martyniuk, T.J. Ronningen, S. Krishna, M. Motyka, *Investigating the physics of higher-order optical transitions in $InAs/GaSb$ superlattices*, Physical Review B, 2021, 104 (8), 10.1103/PhysRevB.104.085410, (IF = 3.7, MNiSW Points: 140)

PATENTS

National Patent Application P.454229, dated 23/12/2025, Robert Tomala, Paweł Głuchowski, Daniela Kujawa, Katarzyna Hałubek-Głuchowska, „Zastosowanie kropek węglowych do zabezpieczenia przedmiotów przed fałszerstwem” (“The use of carbon dots to protect items against counterfeiting”)

RESEARCH STAYS

07/2021 – 10/2021 & 03/2023 Helmholtz – Zentrum Hereon (Germany)

Fabrication of layers made of ferrite and ytterbium and erbium oxide doped with ytterbium and erbium ions using the Plasma Electrolytic Oxidation (PEO) method. Structural studies (XRD, SEM, EDS) and their analysis.

01/2022 Vilnius University (Lithuania)

Fabrication of ferrite nanotubes.

06/2024 University of Aveiro (Portugal)

Atomic force microscopy (AFM) and magnetic force microscopy (MFM) studies of layers made of ferrite and ytterbium and erbium oxide doped with ytterbium and erbium ions using the PEO method.

PARTICIPATION IN CONFERENCES

1. 19th International Conference on Luminescence, 26-30/07/2021, Changchun, China, *Effect of graphene addition on the thermal and persistent luminescence properties of the $Gd_{2.994}Ce_{0.006}Ga_3Al_2O_{12}$ and $Gd_{2.964}Ce_{0.006}Dy_{0.03}Ga_3Al_2O_{12}$ ceramics* – POSTER PRESENTATION
2. 65th international conference Open Readings 2022, 15-18/03/2022, Vilnius, Lithuania, *Effect of graphene addition on the thermal and persistent luminescence properties of the $Gd_{2.994}Ce_{0.006}Ga_3Al_2O_{12}$ and $Gd_{2.964}Ce_{0.006}Dy_{0.03}Ga_3Al_2O_{12}$ ceramics* – ORAL PRESENTATION (Presentation Award)
3. 21st International Conference on Dynamical Processes in Excited States of Solids, 4-9/09/2022, Wrocław, Poland, *The influence of modifier on the luminescent properties of carbon dots* – POSTER PRESENTATION
4. International Conference on Excited States of Transition Elements, 3-8/09/2023 Świeradów-Zdrój, Poland, *Influence of chromatographic separation on optical properties of carbon dots* - POSTER PRESENTATION

5. 35th Conference on Surface Modification Technologies, 18-22/09/2022/ Hamburg, Germany, *Preparation of PEO single and multilayer strontium and barium ferrites coatings on magnesium alloys*, POSTER AND ORAL PRESENTATION
6. The 1st International Online Conference on Photonics, 14-16/09/2024, *Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst*, POSTER PRESENTATION
7. The 4th International Online Conference on Materials, 3-6/11/2025, *A Rapid, Green and Cost-Effective Synthesis of pH- and Hydroxyl Group-Sensitive Carbon Dots for Sensing Applications*, POSTER PRESENTATION
8. 9-th International Conference «NANOBIOPHYSICS: Fundamental and Applied Aspects, *A Rapid, Green and Cost-Effective Synthesis of pH- and Hydroxyl Group-Sensitive Carbon Dots for Sensing Applications*, ORAL PRESENTATION
9. The 1st International Online Conference on Photochemistry, 8-9/04/2026, *Carbon dots/TiO₂ hybrids for photocatalytic degradation of drugs in the aquatic environment*, POSTER PRESENTATION

ORGANISING COMMITTEE

1. 8th Workshop on Physics and Technology of Semiconductors Lasers, 13-16/11/2019, Krakow, Poland
2. 21st International Conference on Dynamical Processes in Excited States of Solids, 4-9/09/2022, Wroclaw, Poland

WORKSHOPS

02/2025 – Effective Leader Workshop - led by Business Makers (1 day)

- Communication and team motivation
- Providing feedback
- Development of leadership competencies

03/2024 - Particle size analysis workshop - organized by Anton Paar (1 day)

- Theory and practice of methods: DLS, LD, DIA
- Working with Kalliope analyzers and software
- Application of methods in industrial applications

11.2021 – 06.2022 - Leader Workshop - organized by Łódź Akademicka Foundation (8 months)

- Leadership competencies and teamwork
- Project management and conflict resolution
- Communication and public speaking

OTHER ACTIVITIES

Popularization of science

- Presented a lecture entitled "Persistent Luminescence – a Phenomenon Not Fully Understood, Although Everyone Has Experienced It" - Lower Silesian Science Festival 2022 and at the 2nd High School named after Rev. Jan Twardowski in Olesnica
- Performed chemical demonstrations at the Lower Silesian Science Festival 2024 and 2025

Institutional activities

- 2023-2026 Member of the Scientific Council of ILT&SR PAS

4. Objectives and scope of the work

Interest in nanotechnology has accelerated research on carbon materials in search of structures with high chemical stability, low toxicity, and unique optical properties. CDs, as a relatively new class of nanomaterials, have transformed the approach to luminophore design by enabling broad tuning of their emission through modification of the surface composition. The variability in structure and internal interactions in CDs precludes the adoption of a single model to explain their luminescence. Precise control of specific phenomena, such as fluorescence from STS or CT and RTP (Room-Temperature Phosphorescence) processes, remains a challenge due to the heterogeneity of these materials. An important aspect of understanding the role of their surface functionalization lies in analysing the influence of functional groups and their surroundings on the final optical properties. Research in this field directly leads to the development of inexpensive, eco-friendly, and highly selective optical sensors for detecting environmental changes. At the same time, many aspects of the interaction between CDs and inorganic semiconductors to create photocatalysts with high photocatalytic activity and capable of utilizing visible light remain incompletely explained and understood. CDs, as biocompatible materials, represent an ideal class of materials that could enhance the performance of previously known photocatalysts without increasing their toxicity. Such hybrid materials therefore merit deeper investigation into the mechanisms of interaction between the two components.

The main scientific goal of this dissertation is to clarify the correlation between the surface chemical nature and the photophysical properties of CDs. Simultaneously, an important aspect was determining the mechanisms of interaction at the CDs-analyte interface in sensor systems and at the CDs-semiconductor interface in hybrid systems. In sensor applications, dynamic molecular processes such as reversible protonation/deprotonation and hydrogen bonding interactions at the interface were investigated. In hybrid systems, charge and energy transfer were studied, as well as the impact on the absorption range, photocatalytic activity, and the reduction and oxidation capacities.

The specific research objectives include:

- **Investigating the role of chemical modifiers in emission mechanisms:** The goal was to determine how acidic and alkaline modifiers affect surface passivation and the stabilization of STS and the resulting spectroscopic properties of the nanomaterials. Furthermore, the research aims to obtain structures with high QY and to understand the mechanism underlying this characteristic.
- **Analysis of molecular interactions in sensing processes:** This topic focused on investigating the mechanism of the optical response of CDs to changes in pH and the presence of hydroxyl groups in organic solvents. A key aspect was understanding the dynamic surface interactions that lead to shifts in emission maxima or luminescence quenching.
- **Determining the synergistic interaction mechanism in hybrid photocatalytic systems:** The research focused on explaining how the presence of CDs (including phosphorescent ones) modifies the absorption properties of TiO₂ (a well-known and commonly used photocatalyst) and influences the efficiency of charge carrier separation and the energy transfer process.
- **Evaluating the photocatalytic efficiency in the degradation of persistent organic pollutants:** The experiment was designed to demonstrate the application potential of the developed hybrid materials in the removal of pharmaceuticals (in this case, CBZ, NPX) from aqueous solutions and to show the possibility of their use in visible light.
- **Explaining the role of surface modification and the use of various methods and its impact on the way CDs attach to the semiconductor and create hybrids with effective transfer between them:** The aim was to investigate the effect of synthesis conditions on the charge and energy transfer between components, as well as photocatalytic activity.

To achieve the set goals, the scope of research included:

- **Design and fabrication of nanomaterials:** Preparation of a series of CDs samples with varying surface functionalization, preparation of CDs sensitive to pH changes, and the presence of -OH groups in organic solvents. The next step was the synthesis of hybrid materials consisting of

CDs and photocatalysts. A simple impregnation method was used to combine mesoporous TiO₂ with two types of CDs (fluorescence and phosphorescence), and various impregnation methods were used to combine ZnO with CDs.

- **Comprehensive physicochemical analysis:** Using microscopic techniques (SEM, TEM) and XRD to study the morphology and structure, and sorption methods to assess the textural parameters of the materials.
- **Advanced spectroscopic diagnostics:** Identification of functional groups on the CDs surface using FTIR spectroscopy and detailed luminescence studies, including excitation, emission, and time-resolved measurements.
- **Reactivity and sensitivity studies:** Examination of optical properties over a wide pH range and in the presence of various organic analytes. Additionally, photocatalytic experiments were monitored by high-performance liquid chromatography (HPLC) to quantitatively assess the extent of pollutant degradation.
- **Interpretation and correlation of the obtained experimental results:** the comparison of the obtained data to propose a coherent emission model and photocatalytic mechanism for the studied systems, which allowed for the formulation of the final conclusions of the dissertation.

The research approach used in this study allowed for a precise investigation of CDs, from the precise design of their structures, through in depth analysis of their physicochemical properties, to practical applications in advanced oxidation processes and chemical analytics. The results expand knowledge of photoluminescence mechanisms in carbon nanomaterials and indicate new avenues for developing eco-friendly technologies for environmental remediation and diagnostics.

5. Abbreviations

0D - Zero dimensional

AIE - Aggregation - Induced Emission

CB - Conduction Band

CBZ - Carbamazepine

CDs - Carbon Dots

CPDs - Carbonized Polymer Dots

CQDs - Carbon Quantum Dots

CT - Charge Transfer

DMF - Dimethylformamide

DMSO - Dimethyl Sulfoxide

FRET - Förster Resonance Energy Transfer

FTIR - Fourier-Transform Infrared Spectroscopy

FWHM – Full Width at Half Maximum

GQDs - Graphene Quantum Dots

HOMO - Highest Occupied Molecular Orbital

HPLC - High - Performance Liquid Chromatography

HRTEM - High - Resolution Transmission Electron Microscopy

IR - Infrared

LED - Light - Emitting Diode

LUMO – Lowest Unoccupied Molecular Orbital

Mid-IR – Mid - Infrared Spectra

MOF - Metal - Organic Framework

NPX – Naproxen

PDI - Polydispersity Index

PEG - Polyethylene Glycol

PET - Photoinduced Electron Transfer

PhCDs – Phosphorescent Carbon Dots

PL – Photoluminescence

PTDA - 3,4,9,10 – perylene tetracarboxylic dianhydride

QY - Quantum Yield

ROS - Reactive Oxygen Species

RTP - Room-Temperature Phosphorescence

SEM - Scanning Electron Microscopy

STEM - Scanning Transmission Electron Microscopy

STS - Surface Trap States

SWCNTs - Single - Walled Carbon Nanotubes

TEM - Transmission Electron
Microscopy

TOC - Total Organic Carbon

UV - Vis - Ultraviolet - Visible
Spectroscopy

VB - Valence Band

XPS - X - ray Photoelectron
Spectroscopy

XRD - X - ray Diffraction

6. Scientific background

6.1. History of 0D carbon nanomaterials

Carbon-based zero - dimensional (0D) materials are defined as objects with nanometer size in all three dimensions. They constitute a relatively young but rapidly developing class of nanomaterials [1]. Although various forms of carbon, such as soot and amorphous carbon nanoparticles, have been known and used for centuries, only the development of nanoscience has enabled their unambiguous classification and detailed study of their structures and properties [2,3].

6.1.1. From fullerenes to carbon dots (1985-2006)

The disruptive moment for 0D carbon nanomaterials, which forms the foundation of today's knowledge, was the discovery in 1985. Kroto's research group achieved an important discovery of fullerenes [4]. The identification of the C₆₀ molecule, characterized by a unique, closed, cage-like structure composed entirely of carbon atoms, paved the way for further research in physics and chemistry. The value of this discovery was recognized in 1996, when the Nobel Prize in Chemistry was awarded. The last decade of the 20th century was a time of intense development in research on nanomaterials. The focus was on synthesis techniques and characterization methods. This development enabled an understanding of the correlation between nanometric size, geometry, and specific physicochemical properties [5,6].

Another milestone in carbon nanotechnology occurred at the beginning of the 21st century, when a new class of materials was identified. In 2004, CDs were accidentally discovered as a byproduct during research on the purification of single-wall carbon nanotubes (SWCNTs) via gel electrophoresis. The research was led by Xu's group and focused on the analysis of the peripheral products obtained from the separation of the nanotubes by the laser ablation method [7]. The researchers observed tiny, spherical carbon nanoparticles that exhibited very intense excitation-dependent luminescence. Initially, this phenomenon was attributed to structural defects or impurities; however, precise structural and spectroscopic characterization revealed that the emission mechanism resulted from the nanometric core size and specific surface functional groups.

The formal term "carbon dots" was proposed by Sun et al. in 2006 to refer to luminescent nanoparticles derived from graphitic materials via laser ablation [8]. This research was a fundamental contribution to the development of this field, demonstrating that effective use of these materials depends on appropriate surface passivation. The authors proved that non-functionalized nanoparticles exhibit very low QY. The surface passivation process increased QY, which, upon thorough optimization, reached 10-11%. This discovery enabled the production of CDs with precisely defined spectroscopic properties, thereby initiating the rapid development of bioimaging, sensors, and photocatalysis.

6.1.2. Optimization of carbon dots (2006-2013)

The years 2005-2012 were an important stage in the history of CDs research, focusing on improving the synthesis method and modulating unique spectroscopic properties [8–12]. During this period, both top-down and bottom-up synthesis methods were optimized to achieve better control over particle size, surface chemistry, and reproducibility [13–16]. The major subjects of this research were surface passivation and functionalization, which were necessary for increasing QY. It was also discovered that surface states and structural defects play a dominant role in tuning the emission properties of CDs, and such modifications can effectively quench the non-radiative emission process [17–19]. Simultaneously, advances in materials science have deepened scientists' theoretical understanding of the photoluminescence mechanism. They have succeeded in explaining the phenomenon of excitation dependent emission, linking it to variations in nanoparticle size and diversification of surface energy states [13,18]. An additional advantage of these materials, such as low toxicity and excellent solubility in water, has also contributed to the development of CDs research, making them an promising candidate for applications in medicine, biology, and environmental monitoring [20–24]. This research created a solid foundation for the controlled synthesis and precise tuning of the performance parameters of CDs, which enabled their rapid development and commercialization in the following decades [16,18,25].

6.1.3. Contemporary classification and development of carbon dots

The breakthrough results achieved by Yang's group in 2013 showed that CDs achieved a record quantum yield of up to 80% [26]. This resulted in an increase in interest in these nanomaterials, leading to an increase in new scientific publications. The number of papers

increased from several hundred per year in the first decade of the 21st century to several thousand in the 2020s [27,28]. This dynamic development enabled not only further optimization of optical properties but also a more precise understanding and classification of the intrinsic diversity of 0D carbon materials. This has led to the identification of subcategories differing in core structure, synthesis methods, and properties. Currently, there are three main subcategories of CDs (Fig. 1) [29]. Graphene Quantum Dots (GQDs) are characterized by a crystalline sp^2 graphene structure with dimensions below 10 nm (1-3 atomic layers) and are obtained using top-down methods. Their properties result from edge effects and quantum confinement, which together offer high electrical conductivity. Their main advantages include excellent electronic parameters, and applications include electronics and photovoltaics [30]. Carbon Quantum Dots (CQDs) have a mixed amorphous sp^2/sp^3 structure, are quasi-spherical, and are synthesized via bottom-up or top-down methods, with dimensions below 10 nm. The luminescence mechanisms combine surface trapping with quantum effects, providing high QY and biocompatibility [27]. Ideal for sensors and bioimaging [31,32]. Carbonized Polymer Dots (CPDs) are amorphous carbon polymer residues with dimensions above 10 nm and are produced exclusively by bottom-up methods. Their luminescence arises from surface passivation and polymer residues, and they exhibit excellent water solubility [33]. This type has applications in bioimaging and catalysis [34].

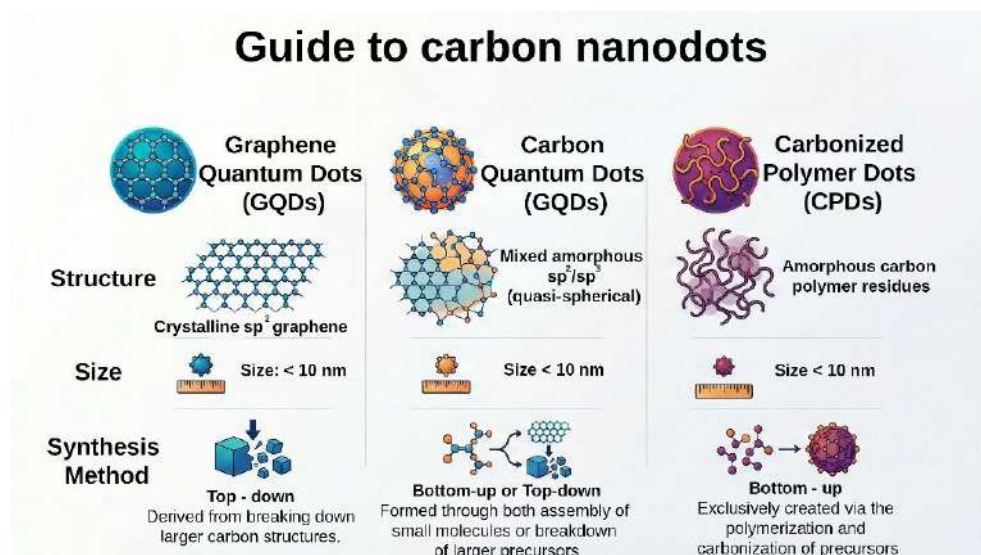


Figure 1. Comparison of the main subcategories of carbon quantum dot materials.

6.2. Synthesis method of 0D carbon nanomaterials

The development of methods for synthesizing 0D carbon materials is a major element in their evolution, enabling control over the core structure, surface composition, nanoparticle size, and QY [8,13,15,18,26]. Currently used approaches are divided into two main categories: top-down methods, which involve the mechanical, chemical, or electrochemical disruption of macroscopic carbon precursors (graphite, nanotubes, graphene), and bottom-up methods, in which nanoparticles are formed through dehydration, carbonization, and condensation of small organic molecules (Fig. 2) [7,13,15]. This division closely correlates with the subcategory classification presented in Fig. 1 - GQDs are obtained primarily via top-down methods, CQDs via mixed methods, and CPDs almost exclusively via bottom-up methods [8,15,16,35].

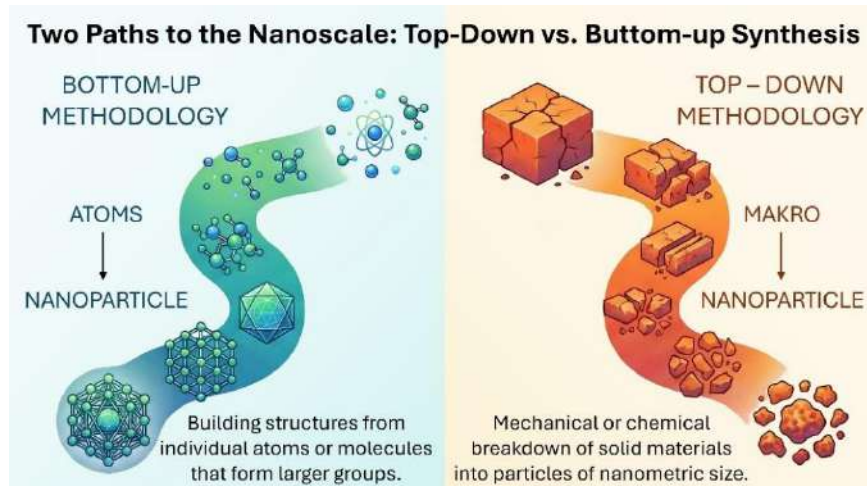


Figure 2. Comparison of synthesis methods of CDs.

6.2.1. Top - down approaches

Top-down methods involve the controlled fragmentation of macroscopic carbon precursors (graphite, graphene, nanotubes) into nanoparticles of 1-10 nm size, while maintaining high sp^2 core crystallinity [14,16,18]. This enables the synthesis of GQDs and CQDs with narrow size distributions (Polydispersity Index (PDI) < 0.3) and emission dependent on defect edge configuration (zigzag/armchair). The bandgap scales according to the $E_g \propto \frac{1}{d^2}$ model, dominating surface effects at $d < 10$ nm [16,18].

The main variants of top-down methods include laser ablation, hydro- and solvothermal cutting in an autoclave, electrochemical cutting, and mechanical fragmentation [14,16,18,36]. Laser ablation can produce graphitic nanostructures and graphene quantum dots with high sp^2 content, but typically at limited yield and strongly process – dependent conditions [17,36–38]. Hydro- and solvothermal cutting in an autoclave often employs oxidants such as $KMnO_4$ or H_2O_2 , where oxidative attack at defect-rich sites and edge regions promotes sheet fragmentation [10,16,39]. Electrochemical cutting by anodic electrolysis of graphite electrodes can generate ROS, including hydroxyl radicals, which contribute to oxidation of graphitic edges and facilitate layer separation; depending on the electrolyte and cell configuration, intercalation and gas evolution may also be major driving forces [14,18,40,41]. Mechanical fragmentation, such as hydrodynamic shearing or ultrasonic cavitation, generates stress on the order of 10^9 Pa, making this method one of the most scalable but with a wider PDI (0.3-0.5) [8,42–44]. In situ surface passivation with ligand blocks non-radiative states, enabling QY.

6.2.2. Bottom - up approaches

Bottom-up methods dominate the production of CQDs and CPDs due to their experimental simplicity, low cost, and industrial scalability [29,34]. They involve controlled dehydration, condensation, and carbonization of molecular precursors rich in C, N, and O, leading to the self-assembly of oligomers via nucleation, core growth, and surface passivation, with the possibility of precise doping with heteroatoms (N, S, P, B) [45,46].

The most versatile hydrothermal technique occurs under typical supercritical/subcritical water conditions (120-300°C, 1-20 MPa, 4-72 h), where precursors undergo H^+/OH^- ion-catalyzed thermal decomposition: from linear/cyclic polymerization to oligomers, through intramolecular condensation forming 2-8 nm aromatic cores, to spontaneous passivation blocking nonradiative states [25,29,35,47]. Solvothermal synthesis (typically 150-350°C, 6-48 h) in organic solvents (DMF, DMSO) increases chemical flexibility, favoring crystalline graphene cores under oxygen-free conditions [29,48,49]. Pyrolysis in a muffle furnace (150–500°C, inert atmosphere) enables a single-step transformation of solid precursors via decarboxylation, condensation, and aromatization, thereby favoring CPDs with excitation-dependent emission [34,50]. Microwave synthesis (commonly 300–800 W, 5–30 min) utilizes dielectric heating to local hotspots ($\sim 1000^\circ\text{C}$), accelerating

nucleation and minimizing aggregation defects [51–53]. A comparison of the representative parameters of the bottom-up methods is presented in Table 1.

Table 1 Comparison of parameters of bottom-up synthesis methods for carbon-based 0D materials.

Method	Solvent	T (°C)	Time (h)	Heating mechanism	Theoretical advantages
Hydrothermal	Water	120 – 300	4 - 72	Convection	Versatile doping, surface passivation
Solvothermal	Organic	150 – 350	6 - 48	Convection	Crystalline cores, hydrophobicity
Thermal pyrolysis	Solvent - free	150 – 500	1 - 12	Conduction	Scalability, one – step
Microwave	Water / organic	120 - 250	0.1 - 0.5	Ionic conduction	Speed, uniformity

6.3. Structural and surface modifications of 0D carbon materials

The optical properties, solubility, and chemical reactivity of 0D carbon materials depend not only on the size and structure of the core (GQDs/CQDs/CPDs), but also on the chemical composition of their surfaces, obtained both during in situ synthesis and through post-synthesis modification processes [29,34,54]. Control over functional groups and the introduction of heteroatomic dopants enable precise tuning of the bandgap energy, increases in photoluminescence QY, and tailoring of surface properties for specific applications, such as bioimaging or sensor technology [10,13,27,55].

6.3.1. Heteroatom doping

The most effective strategy for increasing QY and tuning the emission color is heteroatom doping [46,56,57]. Nitrogen (N-doping) introduced from amine precursors such as ethylenediamine or urea, increases the carrier density and reduces the bandgap energy, enabling Yang and co-workers to achieve QY=80% in 2013 [26]. More advanced multidoping strategies combine nitrogen with sulphur or phosphorus (N+S/P), resulting in a synergistic increase in core polarity, surface-state distribution, and radiative recombination pathways [58,59]. Boron and nitrogen co-doping (B/N) promotes charge

compensation in the carbon lattice, reduces structural asymmetry, and can lead to excitation-independent emission [60,61]. Sulphur or phosphorus doping (P/S) can induce a red shift of the emission because these heteroatoms alter the electronic structure of CDs by reducing the optical bandgap, modifying surface states, and promoting lower-energy $n-\pi^*$ transitions [62–64]. The introduction of heavy atoms (halogens Cl, Br, I) induces the heavy-atom effect, increasing spin-orbit coupling and enabling efficient phosphorescence at room temperature [61,65–67]. Doping is achieved both during synthesis (one-pot with heteroatomic precursors) and post-synthetically via thermal impregnation, with the highest reported QY values (>95%) obtained for N-P-S doped CDs from biomass precursors [68].

6.3.2. Natural functional groups formed during synthesis

Depending on the synthesis method used, the surface of CDs is naturally functionalized with specific chemical groups that determine their colloidal stability and basic luminescent properties. Top-down methods, such as laser ablation or electrochemical cutting of graphene, yield CQDs/GQDs with surfaces primarily composed of carboxyl (-COOH) and hydroxyl (-OH) groups, with a few epoxy groups [14,16,36,38,40]. This ensures good dispersion in polar solvents but limits the QY to low values [9,69]. Bottom-up syntheses, particularly solvo- and hydrothermal and pyrolytic methods, generate a richer set of functional groups, including amine (-NH₂), amide (-CONH-), and ester (-COOR), resulting from the condensation and partial carbonization of organic precursors [35,70,71]. This chemical diversity is responsible for the characteristic excitation-dependent luminescence emission, in which surface states assume the dominant role in the carrier recombination process [72–74].

6.3.3. Surface passivation strategies

A primary step in optimizing the optical properties of CDs is surface passivation of carbon nanoparticles, which eliminates non-radiative recombination and increases QY [8,12]. Currently, multi-step passivation strategies are employed, including neutral polymers such as Polyethylene Glycol (PEG), polyvinylpyrrolidone (PVP), and polysaccharides, which provide exceptional colloidal stability and biocompatibility, silanes and phosphonates, which form stable covalent bonds with the sp² core, and fatty acid salts, which enable fine tuning of surface hydrophobicity [42,69]. Surface passivation enables

QYs above 50% to be achieved, especially with the simultaneous selection of nanoparticle size [18,19].

6.3.4. Post-synthetic modifications and hybridization

The final design step involves post-synthetic covalent modifications on the surface and physical adsorption of targeting ligands [75]. Reactions of carboxyl residues with amines (amide formation: $\text{-COOH} \rightarrow \text{-CONH-R}$) enable conjugation with biologically active molecules, while physical adsorption of antibodies or aptamers achieves targeted drug delivery [76]. Novel approaches include complexation with rare earth ions (Eu^{3+} , Tb^{3+}) that generate white light via mixed Photoluminescence (PL) + RTP emission, hybridization with perovskites for energy conversion, and encapsulation in polymeric micelles to protect against photodegradation [77–79]. The surface properties of CDs depend on the synergistic interaction of the sp^2 core, boundary defects, and the chemical composition of the functional groups [74].

6.4. Physicochemical properties of 0D carbon materials

The diversity of synthesis methods and surface modification strategies described in the previous sections gives rise to a wide spectrum of physicochemical properties in 0D carbon materials. Among these, structure-property relationships at the interface between the core, boundary atoms, and surface functional groups play a main role in defining their optical and electronic behavior [54]. These properties, including characteristic excitation-dependent photoluminescence, RTP, excellent photostability, and unique electronic and surface features, have been systematically investigated in terms of the influence of chemical modifiers on the spectroscopic characteristics [80].

6.4.1. Structural and morphological properties

Structural studies of CDs using TEM and HRTEM, while crucial for characterization, are problematic due to the sensitivity of the carbon material to the electron beam, which often leads to its destruction or measurement artifacts [81,82]. These studies confirm the 0D nature of nanoparticles, with core sizes ranging from 1 to 10 nm, with the morphology closely correlated with the synthesis method and the degree of carbonization of the precursors [13].

GQDs are characterized by a distinctly layered graphene structure (1-3 layers, $d = 0.34$ nm), as evidenced by the crystallographic lattices visible in HRTEM, corresponding to the (002) facets of graphite [16,30]. CQDs exhibit a compact sp^2 network with local sp^3 hybridization domains at the defect edges, while CPDs exhibit an amorphous matrix with remnants of uncarbonized polymer fragments [34,83].

XRD reveals broad diffraction peaks in the $2\theta = 20\text{--}30^\circ$ range, characteristic of disordered graphitization with varying degrees of order, while Raman spectroscopy provides a quantitative measure of defect density through the ratio of the D and G band intensities ($I_D/I_G = 0.8\text{--}1.5$) [84]. These parameters, dependent on the surface chemical composition formed during synthesis or post-synthetic modification, determine the quantum confinement effect and directly influence the position and width of the emission bands [19,56,83,85].

6.4.2. Spectroscopic properties

PL is a dominant feature of 0D carbon nanomaterials, characterized by variable QY ranging from $<1\%$ for unpassivated nanoparticles to $>95\%$ after surface optimization and heteroatom doping [19,56,85,86]. The observed dependence of the emission maximum position and intensity on the excitation wavelength (excitation-dependent PL) arises from the energetic heterogeneity of surface states and the coexistence of multiple carrier recombination mechanisms [54]. Current models describe four interacting PL mechanisms. The first involves core states, in which quantum confinement in an sp^2 crystalline core (GQDs, CQDs, $d < 10$ nm) modulates the emission properties. The emission energy results from $\pi\text{--}\pi^*$ transitions in graphene domains (layer spacing 0.21-0.34 nm) [55]. The second mechanism comprises edge states. Defects at the core edges (zigzag/armchair) create local electron traps [87]. The third involves surface states. Hybridization of the core with functional groups generates chemically specific $n\text{--}\pi^*$ transitions [74]. The fourth consists of molecular states, particularly important in CPDs. Emission here originates from residual polymeric fluorophores, causing broad excitation-dependent bands [34]. This multi-patterning explains the multicolor emission of CDs: blue (450-500 nm, dominated by core states), green (500-550 nm, surface states), and red (600 nm, for large particles or with dopants) [26]. Functional groups may modulate optical properties: --NH_2 increases QY by blocking non-radiative channels and reducing the energy gap [72]. The introduction of heavy atoms (Cl, Br, I) induces the heavy atom

effect, thereby enhancing spin-orbit coupling and enabling RTP [61]. The structural relationships may be confirmed by FTIR, X - ray Photoelectron Spectroscopy (XPS), UV-Vis analyses, and excitation lifetime measurements, providing a basis for the rational design of CDs with given optical parameters [88].

6.4.3. Surface chemistry and colloidal stability

The surface chemistry of 0D carbon materials is largely determined by the presence and chemical nature of functional groups located on their surface [76]. Their identification and analysis are most often performed using FTIR, which enables qualitative determination of bond types and assessment of the degree of surface functionalization [89]. FTIR spectra reveal the presence of hydroxyl, amine, carbonyl, carboxyl, and ether groups, with the intensity and position of the corresponding vibrational bands strongly dependent on the synthesis conditions and the chemical environment [90]. Changes in the protonation state of these groups, induced by factors such as the ambient pH, directly affect the optical properties of CDs, including the nature of absorption and photoluminescent emission [91].

The chemical nature of nanoparticle surfaces is directly reflected in their colloidal stability [42]. One of the parameters describing the stability of aqueous dispersions is the zeta potential, which measures the electric charge at the nanoparticle-dispersion medium interface [92]. The presence of ionized carboxyl or amine groups leads to a negative or positive zeta potential, which determines the electrostatic stability of the system and its resistance to aggregation across a wide range of environmental conditions [93]. These properties are important for both materials processing and potential biological applications [20]. XPS serves as a complementary technique, providing information on the elemental composition and general chemical state of the atoms present on the surface of CDs [94]. Combined with FTIR analysis, it enables a more detailed description of surface chemistry, but FTIR and zeta potential measurements are the fundamental tools in assessing the impact of surface functionalization on the colloidal stability and functional properties of CDs material [52].

6.4.4. Electronic and photoelectric properties

The electronic properties of 0D carbon materials arise from the interplay between the sp^2 carbon core, edge defects, surface states, and the chemical nature of surface functional groups. In contrast to conventional inorganic semiconductor quantum dots, whose electronic structure is primarily governed by periodic crystal symmetry and quantum confinement effect, CDs exhibit a hybrid semiconducting behavior that can be tuned through surface passivation and heteroatom doping. This dual character enables effective modulation of band-edge positions, charge carrier dynamics, and photoresponse, which is important in photocatalysis and optoelectronic applications [1,95].

Photoinduced charge separation in CDs achieves exceptional efficiency in Z-scheme heterostructures (CDs-TiO₂-g-C₃N₄), where the potential difference between the conduction and valence bands drives directional electron transfer from the valence band of the CDs to the conduction band of the acceptors [96]. In contrast to traditional inorganic semiconductors, such as CdSe or CdTe quantum dots (Table 2., Fig. 3.), where the electronic properties are strictly defined by the periodic crystal lattice and quantum confinement, the semiconducting behavior of CDs is a hybrid of the sp^2 core delocalization and surface state contributions [27,97]. While traditional quantum dots are often limited by carrier trapping at uncontrolled surface defects and exhibit Auger-induced blinking, CDs offer superior electronic tunability through precise heteroatomic doping and surface passivation, which effectively stabilizes the band edges and eliminates non-radiative recombination [98,99]. The ultrashort carrier separation time results from charge delocalization in the sp^2 graphene core and minimized radiative recombination at surface defects, outperforming traditional quantum dots due to the unique energetic structure of CDs [100]. This efficiency, modulated by functional group composition and heteroatomic doping, determines the efficiency of photocatalytic processes and photovoltaic cells [101].

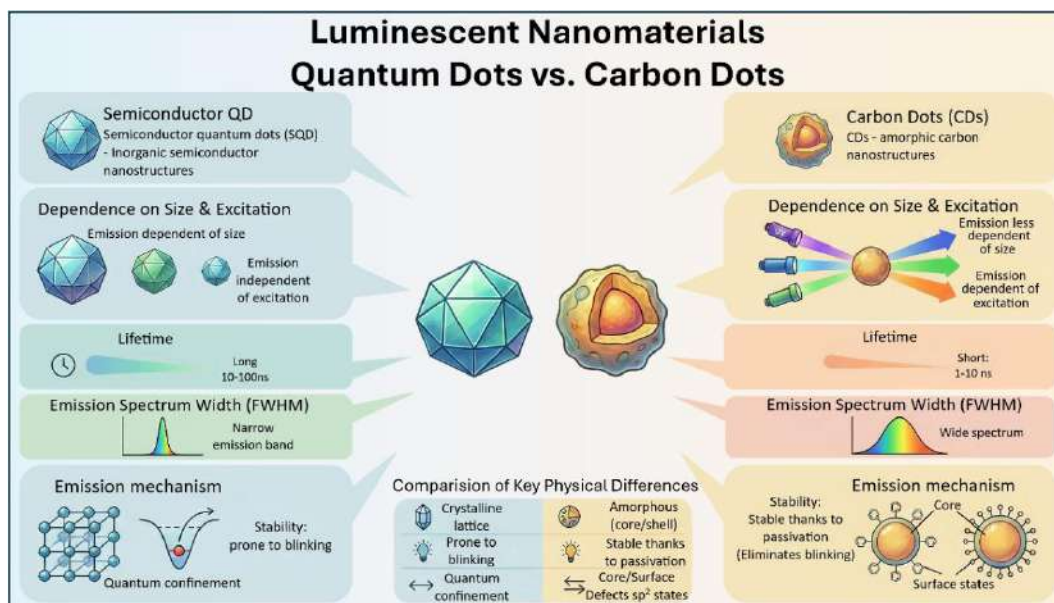


Figure 3. Comparison of the Semiconductor Quantum dots and Carbon Quantum Dots.

Table 2. Comparison of CDs with traditional semiconductor QDs in terms of structure-property relationships.

Properties	CDs/GQDs/CPDs	CdSe/CdTe QDs
Emission tuning mechanism	Surface states + edge states Quantum confinement	Quantum confinement
QY range (%)	1 - 95	50 - 90
Photostability	High (no blinking)	Medium (Auger blinking)
Biocompatibility	High (lack of heavy atoms, benign degradation products)	Low (Cd^{2+} release)
Phosphorescence mechanism	Heavy-atom effect + H-bonding	-

6.5. Application of carbon dots in photocatalysis

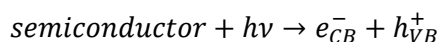
CDs, thanks to their photoelectronic properties discussed in Section 6.4.4 - in particular, their tunable band gap, ultrafast carrier separation, and multilevel energy structure (core, edge, and surface states) are promising components of active photocatalysts in organic pollutant degradation processes [100]. Their ability to effectively utilize visible radiation, generate ROS, and synergize with conventional semiconductors in heterostructures has

been shown to enhance environmental photocatalysis, particularly in the degradation of pharmaceutical drugs resistant to conventional purification methods [102]. However, photocatalytic efficiency depends not only on light absorption, but also on the behavior of the photogenerated charge carriers, which determines whether the system follows an oxidative or reductive pathway through the formation of ROS. In CDs-based hybrid systems, the interfacial structure may control both charge separation and the dominant redox route [103–105].

These properties have been confirmed in numerous studies, where modification of conventional semiconductors with CDs enabled the effective targeting of redox pathways and the removal of difficult contaminants. For example, ZnO nanohybrids with multi-doped CDs (xCDS) exhibit a nearly threefold higher rate constant for photodegradation of CBZ under UV-Vis radiation, and ZnO/CQDs composites effectively purify the gas phase from benzene and methanol by broadening the absorption of visible light [106,107]. Furthermore, by exploiting the up-conversion luminescence phenomenon, CDs in CQDs/Bi₂MoO₆ composites enabled the photodegradation of rhodamine B and the evolution of hydrogen using near-infrared light [108]. Similar synergistic effects were obtained for TiO₂: CQDs/TNs systems were successfully used to degrade textile dyes and tetracycline, while biocompatible CQDs@TiO₂ composites were used to efficiently photodegrade microplastics in aqueous environments by generating ROS [109,110]. Besides pollutant mineralization, stable CDs@TiO₂ systems also perform well in advanced metal photocatalysis as effective components of selective carbon-heteroatom cross-coupling reactions [111].

6.5.1. General mechanism of photocatalytic processes

Semiconductor photoinduction refers to the process of generating charge carriers (electrons and holes) in a semiconductor material after the absorption of a photon of light. In the context of photocatalysis, it occurs as follows: when a photon with energy equal to or greater than the energy of the energy gap ($h\nu \geq E_g$) is absorbed, an electron from the valence band (VB) is excited to the conduction band (CB), leaving a hole (h^+) in VB. Schematically, this process is written as follows:



The resulting charge carriers, an electron in CB (reducing) and a hole in VB (oxidizing), migrate to the catalyst surface, where they participate in redox reactions with substrates ($O_2 + e^- \rightarrow O_2^{\bullet-}$, $H_2O + h^+ \rightarrow \bullet OH + H^+$). Photoinduction efficiency determines photocatalytic performance, making bandgap engineering and heterostructure essential to minimize electron-hole recombination [112–114].

6.5.2. Reactive oxygen species and redox pathways

ROS, which include hydroxyl radicals ($\bullet OH$), superoxide radicals ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$), are fundamental intermediates in photocatalytic reactions. Their formation on the semiconductor surface is determined by the positions of the material's conduction and valence bands, the presence of functional groups, the degree of surface hydration, and the efficiency of charge carrier transport [115,116]. Oxidation processes occur via direct electron transfer from organic molecules to photogenerated holes or via the generation of $\bullet OH$ radicals from the oxidation of water molecules. Due to their high standard potential, these radicals are responsible for the non-selective degradation of persistent pollutants, such as pharmaceutical residues. Simultaneously, photogenerated electrons participate in oxygen reduction reactions to form $O_2^{\bullet-}$. These molecules can undergo direct surface reactions or be converted to hydrogen peroxide, a source of additional reactive species. The balance between redox pathways depends on the mutual matching of the energy levels of the system's components and the interfacial properties. In heterostructures, the introduction of an active phase in the form of CDs modifies these relationships by acting as electron traps, mediators, or absorption centers. This allows the matrix, depending on the chosen synthesis method and the architecture of the CDs interface, to vary its catalytic profile—from a system favoring oxygen reduction and H_2O_2 synthesis to a material oriented toward $\bullet OH$ radical generation or direct photooxidation [103,106,107].

6.5.3. Theoretical basis of organic pollutant degradation

The degradation of organic pollutants in photocatalytic systems proceeds via reactive oxygen species generated at the catalyst surface. Depending on the material and reaction conditions, oxidative degradation may be driven primarily by hydroxyl radicals and photogenerated holes, whereas reduction-assisted pathways may involve superoxide radicals and hydrogen peroxide-derived species [116]. ROS exhibits nonselective oxidative reactivity, attacking all types of organic bonds, regardless of their dissociation

energy [117]. $\bullet\text{OH}$ preferentially initiates the oxidation of aromatic rings via electrophilic addition, whereas $\text{O}_2^{\bullet-}$ reduce heteroatomic bonds (amides, sulfonamides) via single-electron transfer processes (Fig. 4) [118].

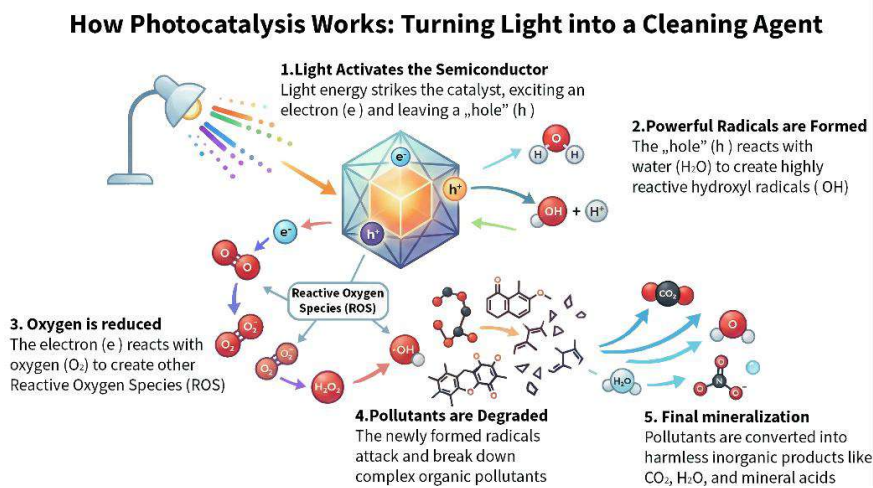


Figure 4. Schematic diagram of the photocatalytic process leading to the degradation of organic pollutants.

The nonselective action of ROS leads to the complete mineralization of organic pollutants into carbon dioxide, water, and simple inorganic anions [30]. First-order kinetics follow the Langmuir-Hinshelwood model:

$$r = \frac{kKC}{1 + KC} \approx k_{app}C$$

where $k_{app}=kK$ represents the apparent rate constant, which depends on the substrate adsorption mechanism on the catalyst surface, the adsorption equilibrium constant, and the internal kinetics of the redox reaction K – adsorption constant, C – pollutant concentration [119]. Organic contaminants, including pharmaceuticals, are resistant to conventional purification methods due to their stable aromatic rings, quinolone scaffolds, and heteroatomic functional groups. Photocatalysis enables their degradation through the simultaneous action of various ROS [116]. Specifically, hydroxyl radicals preferentially oxidize aromatic and heterocyclic structures, while superoxide radical primarily target and cleave heteroatom bonds [115]. Complete mineralization occurs through the sequential degradation of intermediate products, eliminating the toxicity of metabolites typical of biological treatment processes [120].

6.5.4. Hybrid Photocatalysts with CDs

In hybrid materials based on photocatalysts and CDs, the nature of interfacial contact influences the redox pathway. A strong bond between CDs and the semiconductor surface facilitates charge transfer and enhances oxidation and reduction reactions. The design of such systems requires consideration of the possibility of increasing the absorption range of CDs and of their ability to control the formation and reactivity of ROS [121,122].

Synergistic coupling of CDs with conventional broadband photocatalysts such as TiO_2 , $\text{g-C}_3\text{N}_4$, or BiVO_4 , and 2D structures such as graphene or MXene, dramatically improves photocatalytic efficiency through mechanisms including spectral photosensitization, charge dynamics optimization, ROS generation, and cocatalyst function [100,108]. In this role, the CDs or 2D structures provide additional active sites for redox reactions. They promote the efficient separation of photogenerated electrons and holes. They also accelerate the transfer of charge carriers from the primary photocatalyst (TiO_2 , $\text{g-C}_3\text{N}_4$, BiVO_4) and stabilize reaction intermediates. These effects collectively lead to a higher photocatalytic rate and selectivity [122,123]. CDs, thanks to their narrow band gap with multilevel electronic structure (π - π^* transitions, edge defects, n - π^* surface), extend the spectral response to visible light (>400 nm) [17].

6.5.5. Interface charge transfer and heterostructure formation

The interfacial CT formed between CDs and conventional photocatalysts or 2D structures determines the formation of advanced heterostructures with tailored band alignment. Depending on the relative position of the band edges and the nature of the interfacial contact, these systems can operate as Z-scheme, Type-II, or S-scheme photocatalysts, each offering distinct advantages in terms of charge separation and redox power [124,125].

In Z-scheme heterostructures, the recombination of lower-energy electrons and holes occurs at the interface or via a graphene-based mediator, while the most reducing and oxidizing carriers are retained in separate components. This structure maintains a high redox potential for both water oxidation and reduction, enabling efficient water decomposition and pollutant degradation. The CDs or 2D mediators enhance interfacial

conductivity and facilitate vectorial charge transfer, minimizing back-recombination and extending carrier lifetimes [104,126].

In Type II heterostructures, the band edges of the two components are misaligned in a staggered configuration, leading to a cascade of spatial separation between electrons and holes. Electrons accumulate in the more reducing component, whereas holes migrate to the more oxidizing one. This spatial separation prolongs the lifetime of photogenerated carriers and improves the probability of surface redox reactions. However, the thermodynamic driving force for both the reduction and oxidation steps may be somewhat weaker than in Z- or S-scheme systems [124,125].

In S-scheme heterostructures, direct contact between a reducing photocatalyst and an oxidizing photocatalyst is combined with an internal electric field at the interface, which selectively drives charge recombination of the less useful carriers. The remaining electrons and holes are retained in the components with higher reducing and oxidizing power, respectively. The CDs or 2D structures act as charge mediators and interfacial modifiers, accelerating ultrafast CT and stabilizing the desired band bending. This architecture effectively combines strong redox capabilities with efficient carrier separation, making S-scheme CDs-based photocatalysts particularly attractive for visible-light-driven reactions [96,127,128].

6.5.6. Localized ROS generation by CDs in photocatalytic systems

CDs not only serve as efficient light absorbers and charge mediators but also act as generators of ROS in the immediate vicinity of the catalytic interface. Their unique electronic structure and surface chemistry enable the formation of highly oxidizing and reducing species directly at or near the active sites, which is important for photocatalytic degradation and selective oxidation processes [129,130].

Under visible or UV light, CDs generate $\bullet\text{OH}$ at surface defects and functional groups, where trapped holes or highly oxidizing species react with water or adsorbed OH^- [64]. This process is enhanced by the π -adsorption of organic substrates on the sp^2 -hybridized domains of the CDs, a phenomenon driven by non-covalent interactions between the delocalized π -electron density of the adsorbate molecules and the graphitic regions of the CDs. Specifically, the π -electron systems of aromatic or conjugated molecules interact

with the graphitic sp^2 regions of the CDs through π – π stacking, which is driven by London dispersion forces and electrostatic interactions between the co-planar molecular structures. This physical adsorption concentrates the reactants in the immediate vicinity of the ROS-generating sites, thereby increasing the effective concentration of radicals. The spatial proximity between the adsorbed substrate and the generated $\bullet OH$ increases the probability of radical-substrate encounters and improves the reaction rate during photocatalytic degradation [129,131,132].

$^1O_2$ is produced via triplet energy transfer from excited states of the CDs to ground state molecular oxygen, a process enhanced by the presence of heavy atoms of triplet-promoting surface ligands. The CDs therefore act as efficient photosensitizers for $^1O_2$ generation, which is particularly relevant in selective oxidation and photodynamic-type reactions [129]. Concurrently, the hydrophilic-hydrophobic microenvironment at the CDs-semiconductor or CDs-solution interface facilitates substrate enrichment and local accumulation, further amplifying the local ROS concentration and reaction efficiency.

As cocatalysts, CDs act as electron traps with high π mobility, meaning that photogenerated electrons can move efficiently along the sp^2 -hybridized, graphitic domains of the CDs. This π -conjugated network provides a low-resistance pathway for charge transport, stabilizing transient intermediates of water oxidation and other redox steps [80,131–133]. The enhanced mobility of electrons within the π -system suppresses charge recombination and facilitates the formation of energetic cascades that compensate for the wide band gap and poor visible-light activity of conventional semiconductors [133,134]. These features position CDs-based hybrids as a versatile and promising class of photocatalytic materials for environmental and energy-related applications [88][101].

6.6. Application of carbon dots in sensing environmental factors

CDs, thanks to their complex energetic structure comprising a coexisting graphene core, states associated with the edges of the carbon structure, and surface states, exhibit the unique ability to dynamically modulate photoluminescence in response to changes in the surrounding chemical composition [54]. This property, resulting from the ease of oxidation/reduction of functional groups on the CDs' surface and their tunable redox potentials (highest occupied molecular orbital (HOMO) / lowest unoccupied molecular orbital (LUMO) tuned by heteroatomic doping), enables the selective detection of heavy

metal ions, pH gradients, and alcohols [80,135]. Current knowledge highlights the advantage of CDs over traditional organic probes due to their multiparametric response (radiometric fluorescence, lifetime changes, RTP) and the lack of photobleaching under physiological conditions [55].

These properties are reflected in specific sensor systems, where carbon dots demonstrate high sensitivity to environmental conditions. In the area of heavy metal detection, highly fluorescent nitrogen-doped carbon dots (NCDs) were implemented as fluorescent sensors for the selective determination of toxic mercury ions (Hg^{2+}) by quenching their emission in beverages, achieving a high QY (67.4%) [136]. In the analysis of pH gradients, carbon dots derived from o-phenylenediamine, and tryptophan were used to construct a dual-mode colorimetric-fluorescent sensor with a wide operating range (pH 2.2-12.0) [137]. Furthermore, advanced sensor arrays based on fructose and p-phenylenediamine CDs allow for the assessment of pH and freshness of milk samples [138]. The pH dependence of emission parameters was also demonstrated in studies of fluorescence lifetime and intensity for a series of solvothermally synthesized dots, confirming signal stability regardless of photobleaching [88]. In the context of alcohol detection and monitoring the chemical environment, aqueous CDs solutions have been implemented for reversible tracking of the water-ice phase transition and as sensors for alcohol vapors (methanol/ethanol) operating based on the mechanism of alternating quenching and activating luminescence [139]. Furthermore, the high sensitivity of the electronic structure of CDs allows for their selective tuning (solvatochromism) and applications in non-enzymatic glucose detection (via boric acid functionalization) and hormone (hydrocortisone) determination in food using dual-emission sensors. [140–142]

6.6.1. Detailed mechanisms of fluorescent analyte recognition

Most fluorescence sensors based on CDs operate via photoinduced electron transfer (PET), in which the analyte is detected through quenching of the CDs fluorescence [12]. When the CDs absorb an excitation photon, an electron is promoted from HOMO to LUMO. In CDs, the HOMO is often associated with $n-\pi^*$ surface states of carbonyl and amino groups, whereas the LUMO corresponds to the π^* state of the graphene-like core. In the absence of an analyte, this excited electron can recombine radiatively with the hole left behind HOMO, resulting in fluorescence emission [74].

In the presence of an oxidizing analyte, the excited electron can instead tunnel from LUMO of the CDs to an appropriate redox level on the analyte molecule. This nonradiative pathway competes with radiative recombination, so fewer photons are emitted, and the fluorescence intensity decreases (fluorescence quenching) [143]. The efficiency of this PET-based sensing depends on the thermodynamic favorability of the electron transfer [12].

6.6.2. Förster Resonance Energy Transfer (FRET)- Radiometric Sensors

In FRET systems, CDs act as energy donors, transferring energy to acceptor chromophores when the two are positioned at an appropriate intermolecular distance (typically a few nanometers) [144]. The energy transfer occurs via a non-radiative dipole-dipole coupling mechanism, so that the CDs' excited state is quenched while the acceptor emits fluorescence at its characteristic wavelength. In the presence of an analyte, the structure of the donor-acceptor FRET assembly is disrupted – for example, by competitive binding, conformational change, or dissociation of a recognition unit. This leads to an increase in the CDs fluorescence intensity (because energy transfer to the acceptor is suppressed) and a simultaneous decrease in the acceptor's emission (because fewer donors excite it). The resulting change in the ratio of donor to acceptor fluorescence generates a radiometric signal that is largely independent of external factors such as excitation intensity or sensor concentration [142,145].

The efficiency of FRET is governed by the spectral overlap between the emission spectrum of the CDs and the absorption spectrum of the acceptor, as well as by the distance and relative orientation of the donor-acceptor pair. By designing CDs with emission spectra that strongly overlap the acceptor's absorption band, the FRET signal can be tuned to be highly sensitive to small changes in analyte concentration, enabling precise and radiometric monitoring of the target species [142,144,145].

6.6.3. pH sensors - proton modulation of CD surface states

CDs-based pH sensors exploit proton modulation of surface states to enable precise detection across the broad pH range of 1-14, making them highly valuable for monitoring biological, chemical, and industrial environments. This mechanism relies on the reversible protonation/deprotonation of functional groups such as carboxylic (-COOH)

and hydroxyl (-OH), which predominate on CDs surfaces and directly influence their optical properties, particularly fluorescence emission spectra. In acidic conditions, protonation of functional groups, e.g., -COOH, stabilizes lower-energy surface states, resulting in a red shift of the emission maximum and quenching of fluorescence intensity due to enhanced non-radiative energy dissipation. As pH increases, deprotonation yields -COO⁻, altering the local charge distribution, elevating surface state energies, and producing a blue shift in the emission peak – typically 20-50 nm – along with a marked increase in fluorescence intensity due to more efficient radiative decay [137,146].

The wide 1-14 pH sensitivity arises from the heterogeneity of surface groups on CDs, thereby facilitating multi-stage state switching without nanoparticle degradation, ensuring high reversibility (>95% over multiple cycles) and rapid responses [147]. These attributes support radiometric detection, where the ratio of dual emission band intensities exhibits linear pH dependence, minimizing errors resulting from changes in probe concentration [91,148].

6.6.4. Surface Hydrogen-Bond Sensors - Hydrogen Interactions and Surface Structure Perturbations

Alcohol detection is based on perturbations of the hydrogen structure of the CDs surface through competitive hydrogen bonding and catalytic dehydration [75]. Alcohols compete more strongly than water for hydrogen bonding with the -COOH/-OH groups, weakening the H-bonding cross-links responsible for Aggregation-Induced Emission (AIE) and destabilizing CD oligomers. The mechanism of specificity results from steric and electronic differences: smaller alcohols penetrate deep into the surface layers, creating a three-dimensional H-bonding network; larger alcohols cause surface perturbations [149].

N-doped CDs increase selectivity by substituting hydrogen for nitrogen in the -NH-R groups, where the alcohols protonate weak pyridine bases [135,150,151]. Catalytic dehydration activates Lewis's acid defects on the CDs, converting the primary alcohols into aldehydes, which additionally absorb excitation light. The resulting oxidation products permanently modify the surface, causing irreversible long-term quenching [135]. Dual ethanol/pH sensors exploit competition: ethanol blocks AIE at alkaline pH, enabling distinction from pure pH change. These sensors operate in complex matrices with high selectivity for interfering species [140,150,151].

7. Experimental methods

7.1. Synthesis

CDs described in publication **P1** were prepared using two distinct bottom-up synthesis approaches. To investigate the influence of various functional groups on spectroscopic properties, the solvo and hydrothermal method was used. The synthesis was based on research of Liu et al., who used PTDA (98%, Alfa Aesar), distilled water, and triethylamine (99%, Alfa Aesar), and then carried out the reaction in a sealed Teflon reactor placed in a dryer at 220 °C for 48 h [152]. It was the reference sample. To introduce additional functional groups, additional reagents were added as shown in Table 3. These materials were incorporated at 10% by weight or substituted for water, as with DMF. All compounds were purchased from Alfa Aesar.

Table 3. Chemical composition of the solution used to obtain the reference sample and modified CDs.

Name	Modifier	Precursors
		PTDA + triethylamine + ...
CDs	-	H ₂ O
CDs_DMf	DMF 99.8%	DMF
CDs_CA	Citric Acid 99.5%	H ₂ O + CA
CDs_PA	Phosphoric Acid 85%	H ₂ O + PA
CDs_SA	Sulphuric Acid 97%	H ₂ O + SA
CDs_AA	Acetic Acid 99%	H ₂ O + AA
CDs_U	Urea 99%	H ₂ O + U
CDs_EtOH	Ethanol 96%	H ₂ O + EtOH
CDs_EDA	Ethylenediamine 99%	H ₂ O + EDA
CDs_ETA	Ethanolamine 99+%	H ₂ O + ETA

The obtained colloids were then purified by using a membrane filter (CHEMLAND) with a pore size of 0.22 µm.

The CDs used as sensors, described in publication **P2**, were synthesized via a simple, green pyrolysis of citric acid, urea, and sodium hydroxide at 260 °C for 5 hours.

In publication **P3**, two types of CDs and two types of TiO₂ were synthesized. The first type of CDs used as a reference sample was prepared with the method described in publication **P1 without a modifier**. The second type of CDs was phosphorescent and synthesized following the method reported by Ding et al [153]. Citric acid (anhydrous, POCH) and boric acid (99+%, Chempur) were dissolved in water and heated to 180°C for 5 hours.

TiO₂ was obtained using two synthesis methods. The first approach yields an anatase microporous TiO₂ structure via a solvothermal procedure. In this process, titanium(IV) butoxide (97%, Sigma-Aldrich) was added dropwise to acetic acid (99.5-99.9%, Avantor Performance Materials Poland S.A.). The white suspension was placed in a sealed Teflon reactor and dried at 200 °C for 24 hours. After that, the suspension was centrifuged to obtain the product, which was then washed three times with ethanol and dried. The white powder was calcined at 400 °C for 30 minutes.

The second approach allows for the synthesis of mesoporous TiO₂ with an anatase structure. This process is based on the thermal decomposition of a titania based MOF. The precursor MIL-125(Ti)-NH₂ was prepared by dissolving 2-aminoterephthalic acid (90%, Sigma Aldrich) in DMF (Avantor Performance Materials Poland S.A.), and further addition of titanium (IV) isopropoxide and methanol. The solution was placed in a sealed Teflon reactor and heated in a dryer at 150 °C for 24 hours. The MIL-125(Ti)-NH₂ framework, obtained thereafter, was ground in an agate mortar and calcined at 380 °C for 5 hours.

In publication **P4**, CDs were synthesized according to the method described in P1, using DMF as a modifier. Zinc oxide was synthesized by the precipitation method: 5 g of zinc acetate and 100 mL of distilled water were stirred at 60 °C until completely dissolved. To obtain a solution pH of 7–8, NaOH was added dropwise to obtain the electrostatic point of ZnO. The solution was left for 2 hours at 80°C, and the formed Zn(OH)₂ was centrifuged and washed with water and ethanol and then calcined for 3 hours at 450°C. ZnO impregnation with CDs was performed using five methods. The first was standard impregnation, which involved mechanically mixing ZnO and CDs in water, followed by centrifugation and drying of the precipitate. The second method was also simple impregnation, but it used APTES-modified ZnO, which enabled the introduction of silane groups onto the oxide surface to improve bonding with CDs. The third method,

hydrothermal impregnation, involved combining the components in an autoclave under pressure, forcing permanent bonding of the structures. The fourth method was also hydrothermal impregnation but again used APTES-modified ZnO. The fifth method was electrostatic adsorption impregnation. In this method, the pH of the ZnO suspension was adjusted to 6.5 to obtain positive charges on the ZnO surface, which would combine with the negative charge of CDs. A complete, comparative overview of all these chemical pathways across the publications P1-P4 are illustrated in Figure 5.

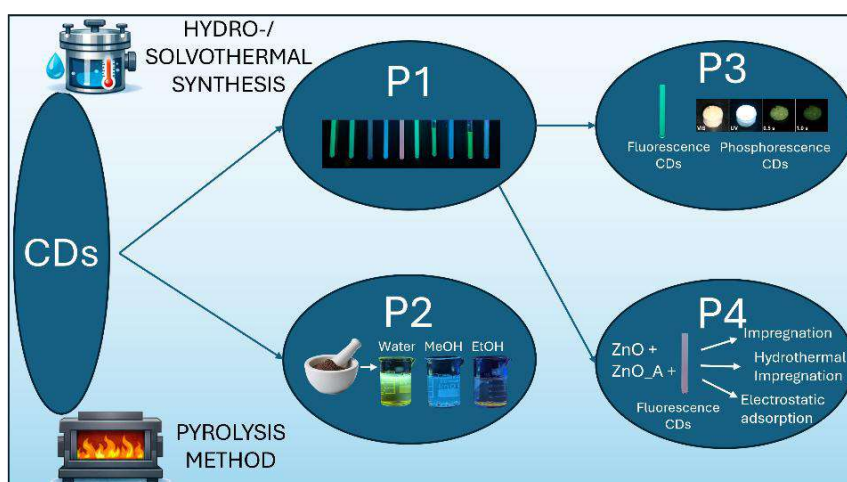


Figure 5. Summary of the synthesis, functionalization and impregnation processes of CDs materials described in research papers.

7.2. Measurement methods and apparatus

Investigation of the crystal structure and morphology

- XRD: data was performed in the angular range $10\text{--}80^\circ 2\theta$ at room temperature using a PANalytical X'Pert PRO diffractometer (Malvern Panalytical, UK). The device was equipped with a copper anode lamp emitting Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$), and measurements were performed with a step size of 0.03° .
- TEM: Morphology analyses were performed using a Philips CM-20 SuperTwin transmission microscope operating at an accelerating voltage of 160 kV. Additionally, a TECNAI G2 20 X-TWIN (200 kV) microscope equipped with a LaB₆ cathode gun, an FEI Eagle 2K CCD camera, and a HAADF detector operating in STEM mode were used.

- SEM: Surface imaging was performed using a Hitachi S-3400N microscope with a tungsten gun and SE and BSE detectors. Pure TiO₂ samples were coated with a gold layer (Cressington 108A sputter coater) and examined at 10 kV.
- Surface area and porosity: Adsorption-desorption isotherms of N₂ were determined at 77 K (Micromeritics 3Flex Surface Analyzer and BSD-660M analyzer). Before the measurement, the materials were activated at 150 °C under a pressure of 1.3 kPa for 12 or 2 hours. The specific surface area was calculated using the BET method, and the total pore volume at a relative pressure of $p/p_0 = 0.9$.

Investigation of the spectroscopic properties

- Infrared and Raman spectroscopy: mid-IR spectra were recorded with a Nicolet iS50 FT-IR spectrometer in KBr pellets or with an ATR module with a diamond crystal (resolution 2 cm⁻¹, range 4000–500 cm⁻¹). Raman spectra were measured on a Renishaw inVia microspectrometer with an excitation line at 514 nm in the range 100–3200 cm⁻¹.
- Absorption and PL: Absorption (reflectance) spectra were collected on a Varian Model 5E UV-VIS-NIR spectrophotometer in the range 200–800 nm (slit width 0.1 nm). The energy gap was determined based on the Kubelka-Munk theory and the Tauc relation. Emission and excitation spectra were recorded on a FLS980 and FLS1000 spectrometer (Edinburgh Instruments) with a 450 W xenon lamp and a Hamamatsu R928P photomultiplier tube. QY measurements were performed using an integrating sphere, using distilled water and DMF as standards.
- Time-resolved measurements: Luminescence decay time measurements were performed using a Libra femtosecond laser (Coherent) with an OPerA-Solo amplifier and a streak camera (Hamamatsu), FLS1000 using pulsed laser diodes with wavelengths of 375 and 450 nm or an Ocean HDX spectrometer with a 330 nm LED as the excitation source.

Photocatalytic activity analysis:

- CBZ degradation: Photocatalytic processes were carried out in a glass reactor with a quartz window (300 W Xenon lamp, UV intensity 30 W/m²). A CBZ solution at a concentration of 14 mg/dm³ was mixed with the photocatalyst (2 g/dm³) at

20 °C. The degradation progress was monitored by HPLC (Shimadzu UFLC LC-20AD) with a PDA detector, and the TOC was measured with a Shimadzu analyzer. Ammonium oxalate, tert-butanol, ascorbic acid, and sodium azide were used as scavengers for the respective radical species in the mechanistic studies.

- Naproxen (NPX) degradation and ROS detection: Photocatalytic reactions were performed at 20 °C in a 25 mL quartz reactor using a 300 W Xenon lamp with an IR filter ($\lambda < 420$ nm filter optionally used). The photocatalyst concentration was 1 g/L, stirred in the dark for 30 min before exposure, with an initial NPX concentration of 15 mg/L. NPX analysis was performed on a Shimadzu LC-6A HPLC with an SPD-M20A detector and a Phenomenex Gemini C18 column, using an acetonitrile/water mobile phase at a flow rate of 0.35 mL/min. Hydrogen peroxide production *via* oxygen reduction reaction was evaluated in a 70% acetonitrile and 30% water with 0.1% formic acid mixture under a 10 L/h airflow, and determined iodometrically using potassium phthalate (0.2 M) and potassium iodide (0.4 M) at $\lambda_{\text{max}} = 350$ nm. For mechanism tracking, hydroxyl radicals were detected via fluorometric oxidation of coumarin (0.5 mM) at excitation/emission of 332/454 nm, while superoxide radicals were monitored colorimetrically using 4-chloro-7-nitrobenzofurazan (NBD-Cl, 0.5 mM) at 470 nm.

8. Results and discussion

8.1. Articles Published

8.1.1. Impact of acidic and basic modifiers on the optical properties of carbon dots - a strategic approach to synthesizing high quantum yield nanostructures (published)

The first stage of the research described in **P1** aimed to systematically investigate the effect of various acidic, alkaline, and aprotic modifiers on the optical properties of CDs. Unlike previous studies focusing on single dopants, this work introduces a detailed comparison of multiple reagents used in situ during hydrothermal synthesis. These studies established a direct correlation between the type of chemical modifier used and the formation of specific functional groups on the surface, thereby enabling precise control of the emission mechanisms and quantum yield of the resulting nanomaterials.

The research problem addressed in this work was to gain a deeper understanding of how the selection of specific chemical modifiers affects final emission parameters, such as QY and fluorescence lifetimes. This publication hypothesizes that by strictly controlling the reaction through the introduction of various modifiers and the selection of heteroatoms, the luminescence mechanism of CDs can be regulated to shift between core and surface states emission.

To verify the hypotheses, the bottom-up synthesis method proposed by Liu et al. [152] was used. PTDA, a molecule with a highly developed system of conjugated π bonds, was used as the base precursor, providing an excellent starting structure for constructing highly organized carbon core.

The study focused on two primary experimental routes:

- **The acidic modification pathway** - These utilize acids with different dissociation constants to investigate how the presence of acidic groups affects the formation of surface structural defects.
- **The alkaline/nitrogenous modification pathway** - The introduction of nitrogen-rich compounds, including those with an alkaline reaction, was primarily aimed

at doping the structure with nitrogen atoms. Nitrogen, which possesses a lone pair of electrons, is a key element that modifies the band structure of carbon materials.

Publication P1 focuses on the correlation between chemical structure and physical properties. Advanced FTIR spectroscopic analysis revealed a diverse array of functional groups on the surface: from hydroxyl and carboxyl groups in acidic samples to amino and amide groups in nitrogen-modified samples. These groups are directly responsible for the dot's unique optical properties.

The most important substantive part of publication P1 is the discussion of the spectroscopic results, including absorption, excitation, emission, and lifetimes (Fig. 6). Two fundamentally different recombination channels were identified and described.

- **STS - Trapping Mechanism** - In samples synthesized in the presence of strong acids, the dominant phenomenon was emission associated with surface defects. The excess oxygen groups create "energy traps" within the band gap. Instead of direct recombination in the core, photogenerated electrons are trapped in these states, which results in a characteristic extension of fluorescence lifetimes.
- **CT - Charge Transfer Mechanism** - The introduction of nitrogen groups in an alkaline environment fundamentally altered the photophysical mechanism. The nitrogen groups act as strong electron donors, initiating charge transfer processes within the nanostructure. This leads to the passivation of non-radiative states, directing nearly all energy toward photon emission and resulting in a high QY of 80%.

In summary, the P1 publication provides evidence that the luminescence of CDs is a dynamic property arising from interactions between surface chemistry and the core structure. The study successfully demonstrates that:

1. An **acidic environment** favors the stabilization of trap states, which is desirable for applications requiring specific excitonic dynamics.
2. An **alkaline and nitrogen-doped environment** optimizes charge transfer processes, which is crucial for achieving maximum emissive brightness.
3. **Surface passivation** using carefully selected amine groups is the most effective strategy for reducing energy losses.

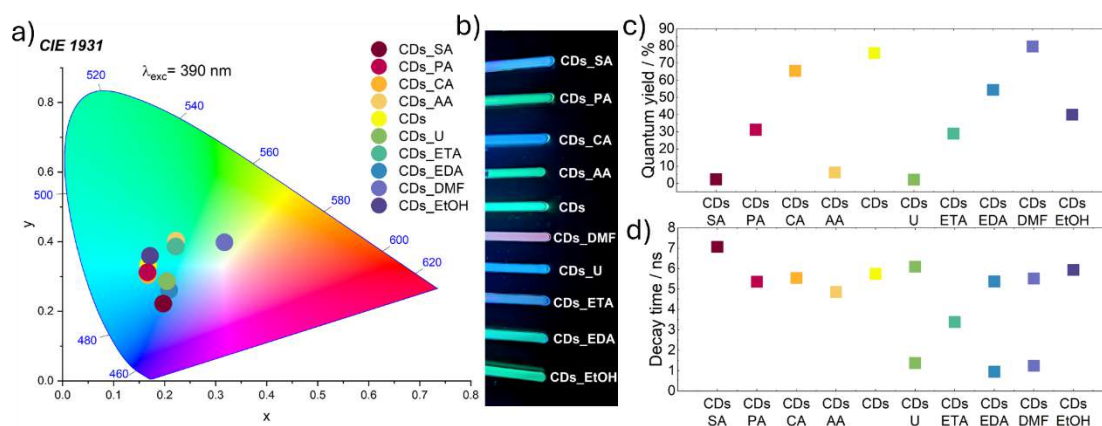
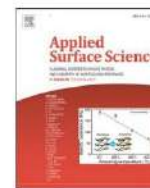


Figure 6. a) CIE diagram of CDs without and with different modifiers under 390 nm excitation, b) image showing the multicolor fluorescence of various CDs samples under a UV lamp ($\lambda_{exc} = 365$ nm), c) the quantum yield of carbon dots with and without a modifier, d) average fluorescence lifetimes of reference and modified carbon dots. Adapted with permission from [154].

These results provide a foundation for further research into how CDs' functional groups behave in various environments and how these interactions affect the optical properties of this material, which is the subject of subsequent publication.

Author contribution to the publication P1

Conceptualization, planning material modifications, synthesis of CDs samples with different modifiers, conducting synthesis, preparing materials for measurements, performing spectroscopic measurements, analyzing the results of spectroscopic and structural measurements, data processing and preparing their graphic visualization, planning the structure of the manuscript, describing the results, preparing the initial and final versions of the manuscript, preparing responses to reviewers, archiving data after preparing the final article



Full Length Article

Tailoring emission mechanisms in carbon dots through controlled surface chemistry

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ABSTRACT

This study examined the effect of selected chemical modifiers on the luminescent properties of carbon dots (CDs). In this case, the CDs were prepared via a hydrothermal method. The precursors used to synthesize this structure were 3,4,9,10-perylene-tetracarboxylic acid dihydride, triethylamine, and various modifiers including aprotic N, N – dimethylformamide, alkaline agents (urea, ethylenediamine, ethanolamine) and acids (sulphuric, phosphoric, citric and acetic acid). This work introduces a novel approach to tailoring the luminescence of carbon dots by investigating the direct influence of various chemical environments during hydrothermal synthesis, demonstrating that aprotic conditions significantly enhance quantum yield, while acidic environments effectively extend luminescence lifetimes by triggering distinct emission mechanisms. To characterize the luminescence changes in the resulting structures, emission, absorption, and FTIR spectra were measured. This characterization demonstrated a correlation between the type of modifier used and the formation of specific functional groups on the dot surface, which also influenced the emission mechanism. Among the alkaline/aprotic systems, CDs DMF exhibited the most pronounced features, achieving an exceptionally high QY exceeding 80%, due to the introduction of donor states and promoted charge transfer (CT) processes. Conversely, acidic modifiers, particularly in the CDs SA sample, were shown to promote surface passivation and stabilization of surface trapping states (STS), resulting in the most extended fluorescence lifetimes (7.07 ns). The presented results confirm the multiple emission center model and indicate the possibility of precisely controlling the optical properties of CDs by selecting the chemical environment of synthesis, providing a versatile platform for high-efficiency bioimaging and optoelectronics sensors.

1. Introduction

Carbon dots (CDs) with a size smaller than 10 nm exhibit great potential as a replacement for semiconductor quantum dots and organic dyes commonly used in various applications, such as drug delivery [1], photocatalysis [2], analytical purposes [3], and even bioimaging [4,5]. These CDs possess advantageous characteristics, including low toxicity [6], low production costs, and high stability [7]. Their desirable properties, including photoinduced electron transfer and excitation-dependent photoluminescence (PL) emission, have led to their widespread utilization in recent years [8]. To explain the luminescence properties of carbon dots, a comprehensive model incorporating three components is necessary: carbon core states, molecular fluorescence, and surface states [8].

The PL mechanism of CDs can be attributed to two factors. First, the quantum confinement effect (QCE) arises due to the nanoscale nature of

carbon dots, resulting in changes in the effective energy separation between ground and emissive states. In carbon dots, this effect becomes significant when the carbon core size is comparable to or smaller than the Bohr radius of the exciton, leading to discrete energy levels instead of continuous bands. As the carbon dot diameter decreases, the distance between discrete energy levels increases, effectively widening the HOMO/LUMO gap. Furthermore, strong confinement of electron–hole pairs in a small volume increases their Coulomb interaction energy, which affects the absorption and emission energies and can alter the photoluminescence efficiency. Second, the presence of surface trap states (STS), influenced by numerous functional groups, also affects luminescence. Liu et al. [9] exhibit that both QCE and STS significantly impact the PL mechanism. QCE modifies the HOMO/LUMO gap width, while surface defects introduce virtual states within this gap, thereby altering the emission energy. The variation in surface groups can be controlled through different synthesis methods and precursors, enabling

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the adjustment of carbon dots' size, physical properties, and passivated surfaces. These parameters also play a role in creating light-emitting energy traps. Covalent modification, which involves introducing new surface groups via covalent bonds and increasing the density of electron clouds, enables adjustments in size and physical properties. On the other hand, non-covalent modification relies on π interactions, electrostatic interactions, or Van der Waals forces between carbon dots and modified precursors. This type of modification does not induce significant structural changes but primarily affects interfacial properties, including quantum yield and photostability [5].

CDs can be synthesized by two main approaches: top-down and bottom-up. Top-down methods involve oxidative or physical cleavage of larger carbon structures such as graphite, graphene oxide, or carbon nanotubes via chemical oxidation, laser ablation, or electrochemical exfoliation. Bottom-up strategies, on the other hand, involve the carbonization of small organic precursors (citric acid, amino acids, or aromatic molecules) using hydrothermal, solvothermal, microwave-assisted, or pyrolytic reactions [10]. Reaction temperature, pressure, and precursor type play a key role in determining the degree of graphitization, domain size, and surface chemistry. High-temperature synthesis typically favors sp^2 -hybridized graphitic domains and narrow emission spectra, while milder conditions lead to smaller amorphous structures with abundant oxygen- and nitrogen-containing groups, which enhance surface solubility and reactivity [11]. Recent advances also include hybrid synthesis methods (e.g., hydrothermal and microwave combinations) and heteroatom doping (N, S, P), which enable fine-tuning of emission behavior and charge transfer efficiency [12].

Surface functional groups play a crucial role in determining both the morphological and spectroscopic properties of nanoparticles. Hydroxyl and carboxyl groups improve water dispersibility and stability through hydrogen bonding, while carbonyl and amine groups contribute to the formation of emission trap states and modify the effective energy separation between ground and emissive states of nanoparticles [13,14]. These chemical moieties can also influence crystallite growth and surface roughness, influencing the overall morphology and photoluminescence quantum yield. Furthermore, changes in surface chemistry can explain the excitation-dependent emission behavior often observed with nanoparticles, as changes in functional group composition or protonation state introduce multiple emissive centers [15–17].

Thanks to their versatile surface chemistry, CDs can easily form hybrid structures with metals, oxides, semiconductors, or polymers. Covalent coupling via amination ($-\text{COOH}/-\text{NH}_2$) or esterification provides robust and conductive interfaces, while noncovalent interactions, such as π - π stacking, hydrogen bonding, or electrostatic attraction, enable reversible association with aromatic dyes, conjugated polymers, or biomolecules. Furthermore, carboxyl and amine groups can coordinate metal ions, enabling CDs to act as chelating agents or electron mediators in catalytic and sensing applications [15]. Encapsulation in polymer or oxide matrices increases photostability and facilitates integration with semiconductor devices. These hybrid architectures not only stabilize luminescence but also extend the functionality of CDs, for example, in photocatalysis or light harvesting systems [18].

The ability to tune the optical and electronic properties of CDs opens a wide range of technological applications. Functionalized CDs have been used in fluorescence sensors, environmental catalysis, bioimaging, light-emitting devices, and energy storage systems [19–22]. Their ability to form chemical bonds with other materials through surface functional groups further enhances their potential in the development of nanocomposites, hybrid photocatalysts, and multifunctional biomedical platforms. Understanding how synthesis parameters and surface chemistry affect their morphology and luminescent properties is therefore essential to optimizing performance in these advanced applications.

In this work, we systematically investigate the effect of various acidic and basic modifiers on the structural, morphological, and optical properties of carbon dots synthesized by hydrothermal methods, using 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTDA) as the main

precursor. During synthesis, a variety of organic and inorganic compounds were employed as surface-modifying reagents, including carboxylic, phosphoric, and sulfuric acids, as well as amine- and amide-containing compounds such as urea, ethanolamine, and ethylenediamine. These reagents were chosen to systematically evaluate the effects of acidic and basic surface modifications. Their incorporation led to the formation of hydroxyl and amine groups, the introduction of additional protons, and the presence of heteroatom-containing functionalities on the carbon dot surface. The novelty of this study lies in the correlation between the type of chemical modifier and the formation of specific surface functional groups, and their subsequent effects on the properties of the carbon dots. While previous studies often investigated single dopants or isolated pH effects, this work presents a comprehensive, direct comparison of multiple acidic and basic modifiers used in situ during hydrothermal synthesis. By combining XRD, FTIR, Raman, UV-Vis, stationary PL measurements, quantum yield, and lifetime, we directly correlate the modifier's chemical composition with the formation of specific surface functional groups and the resulting changes in emission color, quantum yield, and excited-state dynamics. This approach not only contributes to a deeper understanding of the structure-property relationships of carbon nanomaterials but also opens the possibility of their targeted integration in optoelectronic and photonic devices, bioimaging, and sensing applications. The information thus obtained can facilitate the rational design of hybrid materials in which surface-modified carbon dots serve as efficient luminescent components or electron transfer mediators.

2. Experimental section

2.1. Synthesis of CDs

The reference sample was selected as the material synthesized by Liu et al. 26 mg of 3,4,9,10 – perylene tetracarboxylic dianhydride (PTDA) and 98% from Alfa Aesar (Haverhill, United States) were dissolved in a solution of 4 ml of distilled water and 1 ml of triethylamine (TEA), 99% from Alfa Aesar (Haverhill, United States) [9]. The reaction was carried out in a sealed Teflon reactor placed in a dryer with the temperature set at 220 °C for 48 h. After the solvothermal process, the solution was further purified by passing it through a paper filter to separate larger particles from smaller ones. Then, a membrane filter (CHEMLAND) with a pore size of 0.22 μm was used to separate the smallest particles. The modified materials were prepared as reference materials, except that during mixing precursors, in addition to PTDA and triethylamine, additional reagents were added as shown in Table 1. These materials were added at 10% by weight relative to the total mass of the reference system (PTDA + TEA + water). For the CDs DMF sample, a solvothermal approach was applied 4 ml of dimethylformamide (DMF, 99.8%) was used instead of distilled water, creating a polar aprotic environment for the reaction. This modification was intended to investigate the effect of an anhydrous environment and the role of DMF as both a solvent and a

Table 1
Chemical composition of the solution used to obtain the reference sample and modified CDs.

Name	Modifier	Precursors PTDA + triethylamine + ...
CDs	—	H ₂ O
CDs DMF	Dimethylformamide 99.8%	DMF
CDs CA	Citric Acid 99.5%	H ₂ O + CA
CDs PA	Phosphoric Acid 85%	H ₂ O + PA
CDs SA	Sulphuric Acid 97%	H ₂ O + SA
CDs AA	Acetic Acid 99%	H ₂ O + AA
CDs U	Urea 99%	H ₂ O + U
CDs EtOH	Ethanol 96%	H ₂ O + EtOH
CDs EDA	Ethylenediamine 99%	H ₂ O + EDA
CDs ETA	Ethanolamine 99+%	H ₂ O + ETA

surface-modifying agent. All of compounds were purchased from Alfa Aesar (Haverhill, United States).

2.2. Instruments and measurements

The X-Ray diffraction (XRD) was measured between 10 and 80 2 θ degrees at room temperature using a PANalytical X'PERT PRO diffractometer (Malvern Pananalytical, Malvern, UK). The diffractometer uses CuK α_1 (1.5406 Å) radiation with step 0.03°. Mid-IR ATR spectra were recorded using a Nicolet iSTM50 FT-IR spectrometer in ATR mode. Absorption spectra were measured using a Varian Model 5E UV-VIS-NIR spectrophotometer at room temperature in the 200–800 nm range with a resolution of 0.1 nm. Carbon dots' excitation and emission spectra were measured using a FLS980 fluorescence spectrometer from Edinburgh Instruments (Livingston, UK). A 450 W Xenon lamp was used to obtain the excitation and emission spectra, and a Hamamatsu R928P photomultiplier tube (Hamamatsu Photonics, Shizuoka, Japan) was used as a detector. The integration sphere from Edinburgh Instruments (Livingston, UK) was used to measure quantum efficiency. Distilled water and DMF were used as references during quantum yield (QY) measurements. The decay time was measured using a Libra femtosecond laser (Coherent, USA) with an OPerA-Solo parametric amplifier and a Streak Camera (Hamamatsu, Japan) as a detector.

3. Results

3.1. X-ray diffractogram

The XRD pattern indicates that all carbon dots are amorphous (Fig. 1). The results for nearly all samples show a broad band for approximately 22° 2 θ , which can be attributed to the (002) lattice spacing characteristic of disordered carbon [23]. In carbon structures,

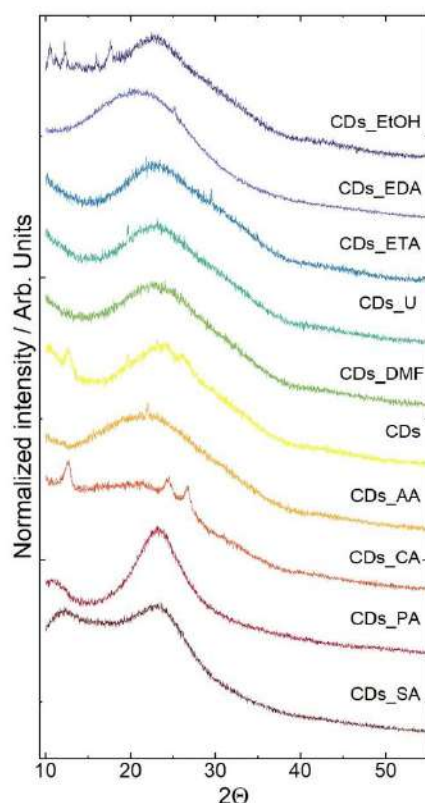


Fig. 1. XRD patterns of reference and surface – modified CDs illustrating the effect of modifiers on their structure.

differences in the maximum intensity and width of bands between samples are mainly attributed to variations in the degree of structural ordering in the carbon core, while differences in interplanar spacing primarily affect the position of the diffraction peaks [24]. Notably, the CDs, EtOH, and CDs_CA results show sharp peaks, suggesting an additional crystal structure in the samples. For CDs_CA additional peaks were observed at 12.76°, 24.52°, and 26.7° (2 θ). The peak at the lowest angle may indicate the presence of a perylene ring structure on the nanoparticle surface, the subsequent peaks are characteristic of reduced graphene oxide and graphite [25]. In CD and CDs_CA an additional peak appears at around 12° (2 θ), which may indicate the presence of oxygen-containing functional groups typical of graphene oxide (GO) or suggest the presence of a fullerene-like structure in the nanoparticle core. The same peak is observed also in CDs_EtOH, but additional peaks can also be indicated at 10.3, 16.11, and 17.6 °C 2 θ . Moreover, CDs_CA exhibit peaks at 24.2° and 26.6°, which are characteristic of graphite. This implies that the core of this sample may consist of multiple carbon forms: graphene, graphene oxide, and graphite [25]. A smaller FWHM corresponds to larger crystallites. Accordingly, the largest graphene domains are found in CDs_PA, while the smallest are observed in CDs_CA and CDs_AA.

3.2. FTIR spectra

Infrared spectroscopy measurements were performed for all synthesized carbon dot samples, which were categorized into three groups: unmodified (reference), modified with acidic agents, and modified with alkaline agents (Fig. 2).

In all samples, except CDs_DMF, a characteristic broad band was observed around 3200 cm⁻¹, assigned to O–H stretching vibrations. This is consistent with the aqueous nature of the synthesis medium, as water contributes significantly to this signal. In contrast, CDs_DMF, synthesized in the absence of water, exhibited only weak O–H absorption and showed distinct low-intensity bands at 2850 and 2930 cm⁻¹, characteristic of aliphatic C–H stretching.

The region between 1000 and 1800 cm⁻¹ showed the greatest variation among samples. A prominent and consistent absorption band between 1635 and 1650 cm⁻¹, attributable to C=C stretching in the sp²-hybridized carbon core of the CDs, was observed across all samples. A shoulder or secondary peak at about 1550 cm⁻¹, attributed to C=O stretching, appeared in the spectra of CDs modified with AA, CA, and U, where carbonyl groups are known to be present. Although DMF also contains a C=O group, its strong overlapping C=C signal likely masks the carbonyl band. In the 1300–1500 cm⁻¹ range, multiple bands were detected, generally assigned to C–H bending vibrations. The complexity and multiplicity of these bands suggest interactions with adjacent functional groups, likely due to hydrogen bonding or steric interactions from densely packed surface moieties. Notably, CDs_SA and CDs_PA exhibited strong absorptions in this region, suggesting the presence of S=O and P=O functionalities, respectively. These functional groups may also contribute to overlapping bands observed in the 2800–3500 cm⁻¹ and 1550–1650 cm⁻¹ regions, where O–H, N–H, C=O, and C=C stretches typically appear. This spectral overlap can obscure contributions from nitrogen-containing functionalities such as amides and amines.

To further elucidate differences among the modified CDs, a comparative analysis of unique IR bands relative to the reference sample (CDs) was conducted. The table (Table 2) below summarizes these unique IR bands (cm⁻¹), detected only in modified samples but absent from the baseline spectrum, which supports the successful incorporation of diverse chemical functionalities:

3.3. Absorption spectra

Spectroscopic analysis of UV–Vis absorption (Fig. 3) revealed distinct absorption ranges depending on the type of modifier used in the

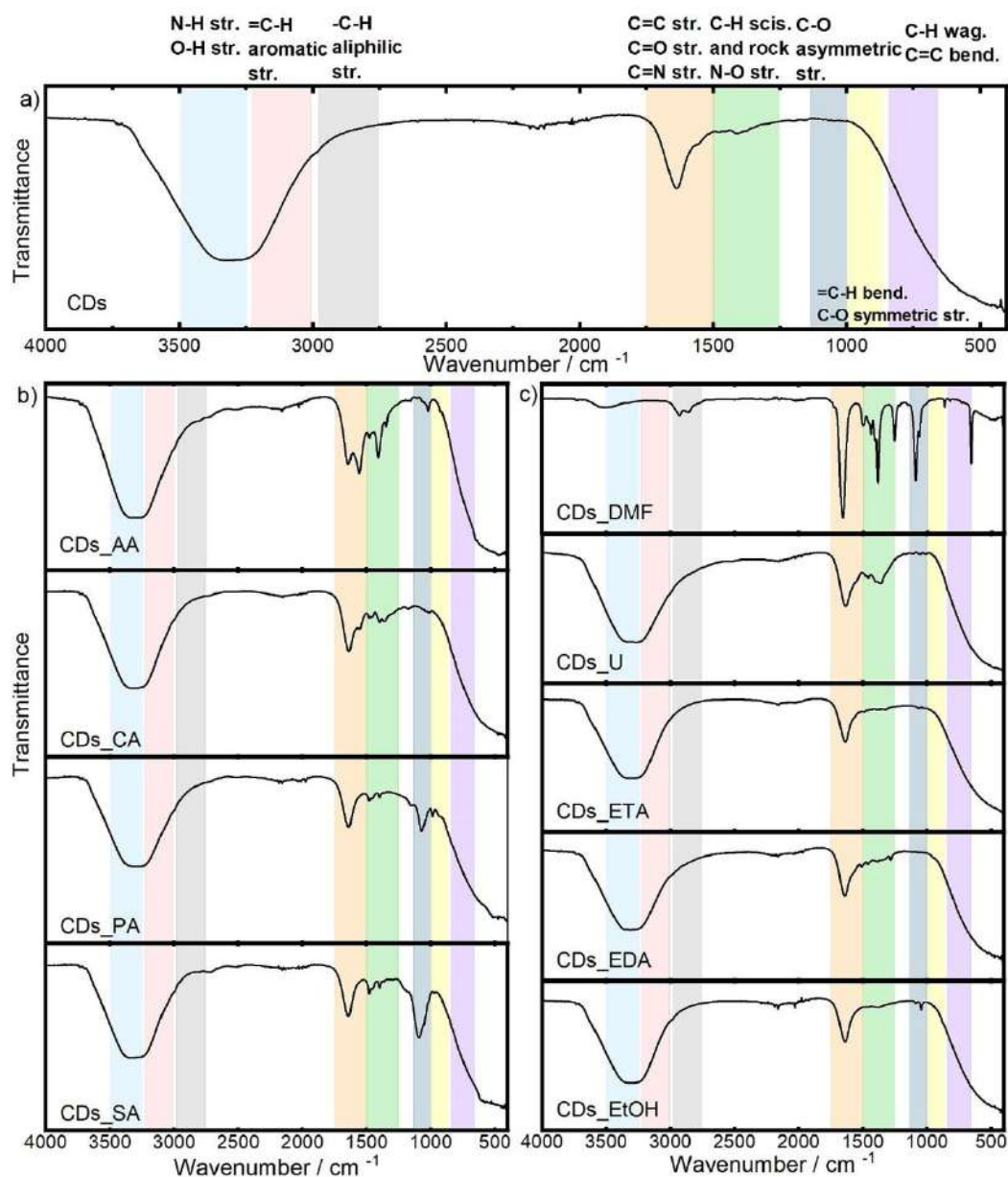


Fig. 2. IR spectrum of CDs a) without and with b) acid and c) alkaline functional groups.

Table 2

Unique IR absorption bands relative to the reference sample (CDs).

CDs Sample	Unique Bands (cm ⁻¹)
CDs_AA	1020.6 (C-O stretching), 1408.7 (C-H scissors), 1556.8 (C=C stretching)
CDs_CA	1398.6, 1477.7 (C-H bending), 1545.8 (C=C stretching)
CDs_DMF	658.1, 864.9, 1063.1, 1090.1, 1255.4, 1385.1 (C-N stretching), 1437.7 (C-H scissors and rocks), 1502.3 (N-O stretching), 2929.3 (C-H stretching), 3503.1 (N-H stretching)
CDs_EDA	1282.4 (C-N stretching)
CDs_ETA	—
CDs_EtOH	1045.2 (C-O asymmetric stretching)
CDs_PA	985.9 (P-OH bending), 1070.8 (P-O-C stretching)
CDs_SA	1089.1 (S=O stretching), 1398.6 (S=O stretching / COO ⁻ stretching), 1478.2 (C=C stretching)
CDs_U	1362.9 (C-N stretching)

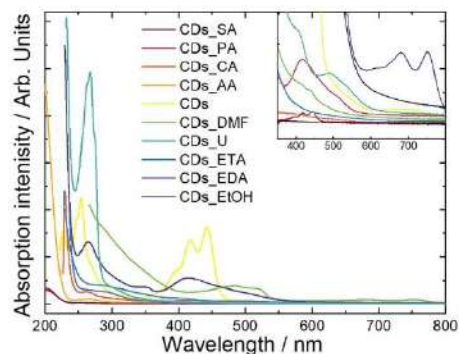


Fig. 3. Absorption spectra of carbon dots without and with different modifiers.

synthesis of carbon dots (CDs). Absorption spectra were recorded in the range of 200–800 nm for all samples. All spectra exhibited characteristic, strong absorption in the ultraviolet region, typically with a maximum between 230 and 280 nm. This band is associated with π - π^* electronic transitions in aromatic C=C systems, commonly attributed to sp^2 -hybridized carbon domains within the core of the carbon dots [26,27].

However, significant differences between samples appear in the 300–400 nm region (Table 3). Many systems exhibit bands characteristic of n - π^* transitions, associated with carbonyl groups or other centers that introduce STS [28]. The presence of these bands indicates varying degrees of oxidation and surface chemistry, resulting from the type of modifier used. In particular, samples prepared with reagents containing nitrogen heteroatoms or compounds that promote surface chemical modification exhibit broadening of signals in this range, indicating the formation of additional electronic states associated with the presence of C-N, N-H, or N-O groups [29].

Differences in the spectra are also visible above 400 nm, where

Table 3

Summary of characteristic UV–Vis absorption features of reference and surface-modified carbon dots.

Sample	λ_{max}	Defect	Donor level	Functional group	Ref.
CDs_SA	200–300 (π – π^*) 300–400 (n – π^*)	QCE, sp^2 Carbon Core STS	S-donor	C=C S=O, C=O	[28,35]
CDs_PA	200–300 (π – π^*) 300–500 (n – π^*)	QCE, sp^2 Carbon Core STS	P – donor	C=C P-O-C, P-OH, C=O	[28,36]
CDs_CA	200–300 (π – π^*) 300–500 (n – π^*) 600	QCE, sp^2 Carbon Core STS Charge transfer /STS	O – donor O – donor	C=C C=O C=O	[28,33]
CDs_AA	200–300 (π – π^*) 300–400 (n – π^*)	QCE, sp^2 Carbon Core STS	O – donor	C=C C=O	
CDs	200–300 (π – π^*) 300–500 (n – π^*)	QCE, sp^2 Carbon Core STS	O – donor	C=C O-H, C=O	[28,33]
CDs_DMF	300–500 (n – π^*) 500–700	STS Charge transfer /STS	N-donor N-donor	C-N, N-O, N-H C-N, N-O, N-H	[28,29]
CDs_U	200–300 (π – π^*) 500–550	QCE, sp^2 Carbon Core Charge transfer /STS	N-donor	C=C N-H, C=O	
CDs_ETA	200–300 (π – π^*) 300–500 (n – π^*) 650	QCE, sp^2 Carbon Core STS Charge transfer /STS	N-donor N-donor	C=C N-H, C-N N-H, C-N	
CDs_EDA	200–300 (π – π^*) 300–400 (n – π^*)	QCE, sp^2 Carbon Core STS	N – donor states	C=C C-N, N-H	
CDs_EtOH	200–300 (π – π^*) 300–500 (n – π^*)	QCE, sp^2 Carbon Core STS	O – donor	C=C O-H, C-O	[28,33]

STS – Surface Trap States, QCE – Quantum Confinement Effect.

absorption is typically associated with surface defect states and local donor centers [10,30]. The presence of signals in this part of the spectrum indicates that selected modifiers—especially those containing nitrogen atoms or acid groups—promote the formation of conjugated surface systems that expand the available energy states [31,32]. The spectra of some samples also extend into the far-visible region, characteristic of a more complex, chemically diverse surface. The comparison of absorption maxima positions confirms that the type of modifier influences the degree of electron delocalization and the nature of surface states in the studied structures. The use of nitrogen-containing compounds leads to a noticeable shift of selected bands toward longer wavelengths, consistent with the presence of donor electronic levels. Acidic modifiers, on the other hand, favor the formation of surface systems with a more complex electronic structure, as evidenced by the presence of additional bands in the visible range [33]. Samples obtained in aprotic solvents such as DMF exhibit the most extensive absorption structure, indicating the formation of a large number of energetically diverse surface centers [34].

The results obtained clearly confirm that the modifiers used significantly influence the electronic structure of carbon dots. Different synthesis conditions lead to different configurations of surface groups, which in turn translate into the diverse nature of electronic transitions observed in the UV–visible spectra. These changes have direct implications for the mechanisms responsible for subsequent luminescent properties, as they shape both the types and distributions of surface states involved in absorption and emission.

3.4. Excitation spectra

The excitation spectra of CDs (Fig. 4), synthesized with different surface-modifying agents, were recorded at selected emission wavelengths ranging from 475 to 540 nm. These wavelengths were chosen based on the observed fluorescence maxima for each sample. For unmodified CDs, three emission wavelengths exhibited the highest intensity. For CDs_DMF, two emission wavelengths were selected, while for the remaining samples, one characteristic emission wavelength was used. The excitation spectra were normalized to the respective intensity maxima to allow direct comparison of spectral shapes and band positions.

The excitation behavior showed a marked dependence on both the nature of the surface modifier and the emission wavelength, arising from the presence of various surface states and emissive centers formed by the introduction of specific functional groups. These surface modifiers alter the electronic structure and energy levels of the dots, leading to distinct pathways and giving rise to excitation-dependent photoluminescence.

Characteristic excitation bands can be assigned to specific electronic transitions (Table 4). The bands observed in the 230–300 nm region correspond to π – π^* transitions of aromatic C=C domains within the sp^2 carbon core [37]. Bands appearing in the range 300–420 nm originate from n - π^* transitions associated with carbonyl, carboxyl, and heteroatom-containing (N, S, P) functional groups, which introduce STS and broaden the excitation profiles [29]. Additional transitions at 420–520 nm reflect the presence of deeper surface states or charge – transfer process, particularly prominent in samples modified with nitrogen – containing compounds (EDA, ETA, U), where donor states introduced by amine or amide functionalities stabilize low-energy channels [29,38]. Samples synthesized with acidic modifiers (SA, PA) exhibit features in the 410–450 nm range linked to defect states associated with S=O, P-O groups, respectively, which effectively modulate the energy of the n - π^* transitions [30,33,39].

These spectral components highlight how specific dopants and functional groups influence the density and energy distribution of surface-localized electronic states. The observed differences between acidic and basic modifiers are consistent with the expected changes in electron delocalization, oxidation state, and trap state structure induced by their respective functional groups [30,37]. The obtained excitation

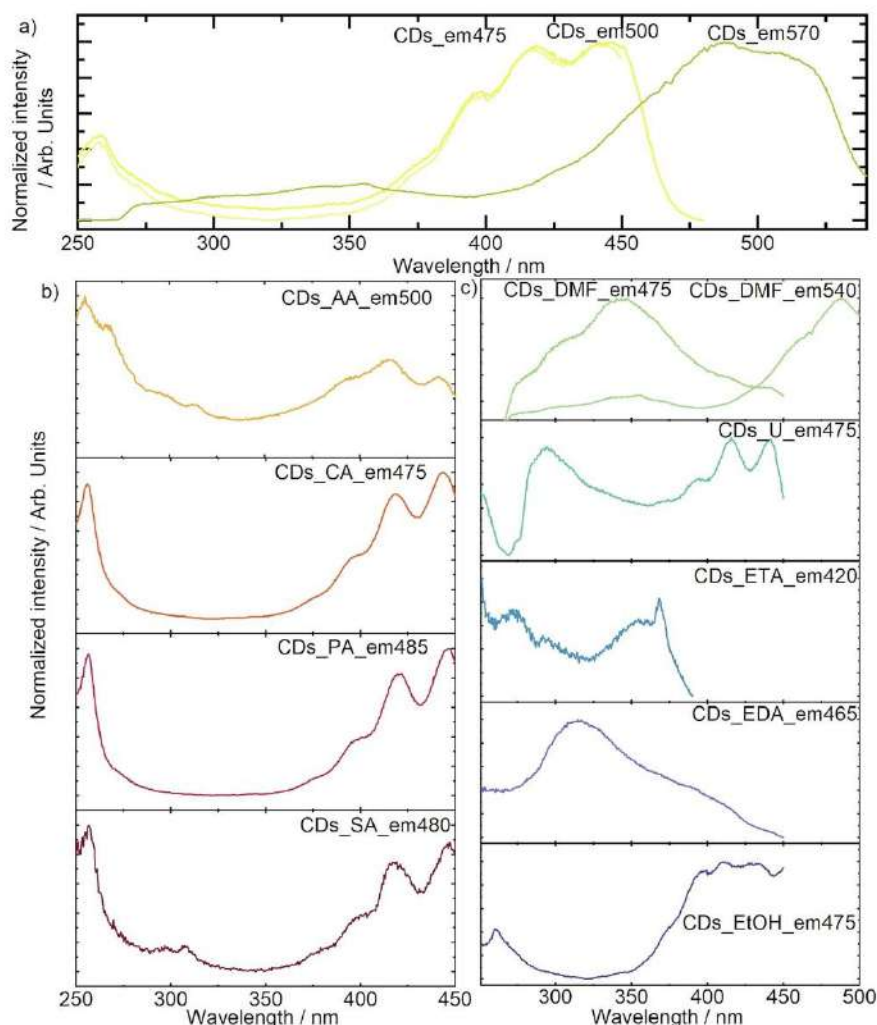


Fig. 4. Normalized excitation spectra of carbon dots a) without and with b) acid and c) alkaline modifiers.

profiles therefore directly reflect the chemical nature of the surface modifiers and their role in determining the photophysical response of the resulting carbon dots.

3.5. Emission spectra

The spectroscopic properties of carbon dots (CDs), both unmodified and modified with various chemical agents, were systematically investigated using normalized and non-normalized fluorescence emission spectra under six excitation wavelengths: 245, 280, 325, 390, 440, and 500 nm (Fig. 5 and S1). These excitation wavelengths were selected based on the samples' absorption spectra to ensure comprehensive characterization. Unmodified CDs exhibited relatively stable emission maxima ($\lambda_{em} \approx 482\text{--}485$ nm) across excitations from 245 to 440 nm, indicating homogeneous emissive centers (Fig. S1). This behavior was also observed for part of the modified samples, including CDs_CA, CDs_EtOH, and CDs_PA, which exhibited wide emission bands with maxima in the 475–500 nm range under the same excitation wavelength. These results suggest that the fundamental emission mechanism was largely preserved in these cases despite surface functionalization. In contrast, several chemically modified CDs showed pronounced excitation-dependent shifts in emission maximum, reflecting increased heterogeneity in emissive states or the introduction of new surface-related energy levels. This effect was especially evident in CDs

modified with EDA, U, ETA, SA, AA, and DMF. For these samples, emission maxima were strongly dependent on excitation wavelength, shifting from the UV-blue region toward the green-yellow as excitation energy decreased. Notably, CDs_EDA showed a progressive redshift in emission maxima: from 350 nm at 280 nm excitation, to 400 nm at 325 nm, then 465 nm at 390 nm, and finally 520 nm at 440 nm, reflecting highly excitation-dependent emissive behavior (Fig. S1). Similar dual-band emission patterns were observed in CDs_U, CDs_AA, and CDs_ETA, particularly under higher-energy excitations (245–325 nm), where emissions centered around 400 and 480 nm were detected. These dual-emission features indicate the coexistence of multiple emissive centers, potentially linked to specific functional groups (e.g., $-\text{NH}_2$, $-\text{OH}$) or charge-transfer states [17,40]. CDs_SA and CDs_PA exhibited especially complex emission behavior. Under 500 nm excitation, these samples displayed broad emission bands peaking around 600 nm, superimposed with narrow, higher-intensity peaks. CDs_PA showed distinct sharp peaks at 310 and 365 nm under 280 and 325 nm excitation, respectively. CDs_SA, on the other hand, exhibited overlapping narrow and broad bands under 325 nm excitation, with broad-band maxima shifting from 385 nm at 325 nm excitation to 445 nm and 515 nm for 390 and 440 nm excitations, respectively. This supports the presence of two distinct emission mechanisms: one broad-band and excitation-dependent, the other narrow-band and likely originating from well-defined emissive sites or defect states [41]. The most complex

Table 4

Summary of characteristic excitation spectra features of reference and surface-modified carbon dots.

Sample	λ_{max}	Defect	Donor level	Functional group	Ref.
CDs_SA	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	[28,35]
	300–400 ($n - \pi^*$)	STS	S – donor	S=O, C=O	
	400–500	STS	S – donor	S=O, C=O	
CDs_PA	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	[28,36]
	300–400 ($n - \pi^*$)	STS	P – donor	P–O–C, P–OH, C=O	
	400–500	STS	P – donor	P–O–C, P–OH, C=O	
CDs_CA	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	[28,33]
	300–400 ($n - \pi^*$)	STS	O – donor	C=O, C–O	
	400–500	Charge transfer / STS	O – donor	C=O, C–O	
CDs_AA	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	[28,33]
	300–400 ($n - \pi^*$)	STS	O – donor	C=O, C–O	
	400–500	STS	O – donor	C=O, C–O	
CDs	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	[28,33]
	300–400 ($n - \pi^*$)	STS	O – donor	C=O	
	400–500	STS	O – donor	C=O	
CDs_DMF	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	[28,29]
	300–400 ($n - \pi^*$)	Charge transfer / STS	N – donor	C–N, N–O, N–H	
	400–500	Charge transfer / STS	N – donor	C–N, N–O, N–H	
CDs_U	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	
	300–400 ($n - \pi^*$)	STS	N – donor	N–H, C–N, C=O	
	400–500	STS	N – donor	N–H, C–N, C=O	
CDs_ETA	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	
	300–400 ($n - \pi^*$)	STS	N – donor	N–H, C–N	
	400–500	STS	N – donor	C–N, N–H	
CDs_EDA	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	
	300–400 ($n - \pi^*$)	STS	N – donor	C–N, N–H	
	400–500	STS	N – donor	C–N, N–H	
CDs_EtOH	200–300 ($\pi - \pi^*$)	QCE, sp^2 Carbon Core		C=C	[28,33]
	300–400 ($n - \pi^*$)	STS	O – donor	C–O	
	400–500	STS	O – donor	C–O	

STS – Surface Trap States, QCE – Quantum Confinement Effect.

emission profile was observed in CDs_DMF, which exhibited four-band emission under 280 nm excitation, with peaks at 390, 455, 535, and 570 nm. As excitation wavelength increased, the relative contributions of these emission bands changed, indicating multiple, independently excitable emissive states [41]. For example, 325 nm excitation still prominently featured the short-wavelength bands, whereas lower energy excitations suppressed their intensity in favor of red-shifted emissions, consistent with the formation of multiple independently excitable emissive states, likely associated with DMF-induced surface

modifications. Quantitative fluorescence measurements at 390 and 440 nm excitation revealed that unmodified CDs and CDs_EtOH showed the highest emission intensities (Fig. 5). CDs_U also maintained relatively strong emissions, while CDs_AA, CDs_SA, and CDs_PA exhibited significantly reduced intensities, likely due to fluorescence quenching or inefficient radiative recombination pathways introduced by their surface chemistries. The emission color coordinates of all samples, as plotted in the CIE 1931 chromaticity diagram (Fig. 6b and S2), further visualized the spectral shifts: unmodified CDs and weakly modified samples (e.g. CDs_EtOH) clustered in the blue-green region, while red-shifted emissions from CDs_DMF, CDs_ETA, and CDs_U shifted their coordinates toward the green-yellow region. The multicolor fluorescence of CDs samples exposed to UV ($\lambda = 365$ nm), recording emission from blue to red in unmodified and modified samples is presented in Fig. 6c.

3.6. Quantum yield (QY) measurements

The presented data clearly demonstrates the significant impact of the applied modifier on the QY of CDs. All measurements were performed at the same concentration, previously selected based on reference as the one that provided the maximum QY for CDs_DMF (Fig. 7). However, as described above, because some components crystallized in the carbon dot solution, the concentration could not always be accurately determined. The highest values were observed for samples without modifiers and modified with CA, and DMF, where the quantum yield exceeded 65%, reaching almost 80% for CDs_DMF. A slightly lower, but still satisfactory result was obtained for CDs_EDA, for which the QY was 54%. For samples CDs_SA, CDs_PA, CDs_AA, CDs_U, CDs_ETA, and CDs_EtOH, the QY was below 40%. These results indicate that the chemical nature of the modifier plays a key role in the photoluminescence emission mechanisms of CDs.

The QY was also studied as a function of concentration for CDs_DMF (Fig. S3). Using a relative method, QY values were determined for a dilution series ranging from high (636 $\mu\text{g}/3$ ml) to very low (2.4 $\mu\text{g}/3$ ml) concentrations. The results revealed a strong inverse correlation between concentration and quantum yield. At concentrations above approximately 150 $\mu\text{g}/3$ ml, significant emission quenching was observed, with QY values consistently below 20%. This quenching is attributed to intermolecular interactions such as aggregation or energy transfer, which promote non-radiative relaxation pathways [42]. As the solution was diluted, the QY increased systematically, reaching a maximum of 79.7% at 2.49 $\mu\text{g}/3$ ml. Further dilution to 2.4 $\mu\text{g}/3$ ml resulted in a slight decrease in QY (72.1%), indicating an optimal concentration window for maximum fluorescence efficiency. These findings highlight the necessity of precise concentration control in applications requiring high fluorescence quantum yield, such as bioimaging or optical sensing in transparent media. Reducing the hydrogen group content in the studied systems increases the emission quantum yield. This is due to the high energy of the O–H bond vibrations, which favors non-radiative relaxation of excited states. Reducing the number of –OH groups reduce vibrational-electron coupling and thus reduces the probability of nonphotonic deactivation, enabling more efficient radiative emission.

3.7. Lifetime measurements

Fluorescence lifetime measurements of CDs modified with different chemical reagents – performed at emission wavelengths individually adjusted to the fluorescence maxima of each sample – showed significant differences in the dynamics of their excited states, which indicates the influence of surface functionalization on the photophysical behavior of these nanostructures (Fig. 8). The reference CDs exhibited a lifetime of 5.74 ns, while the sample modified with SA demonstrated the longest lifetime of 7.07 ns, suggesting effective surface passivation and suppression of non-radiative recombination pathways [37]. Similarly,

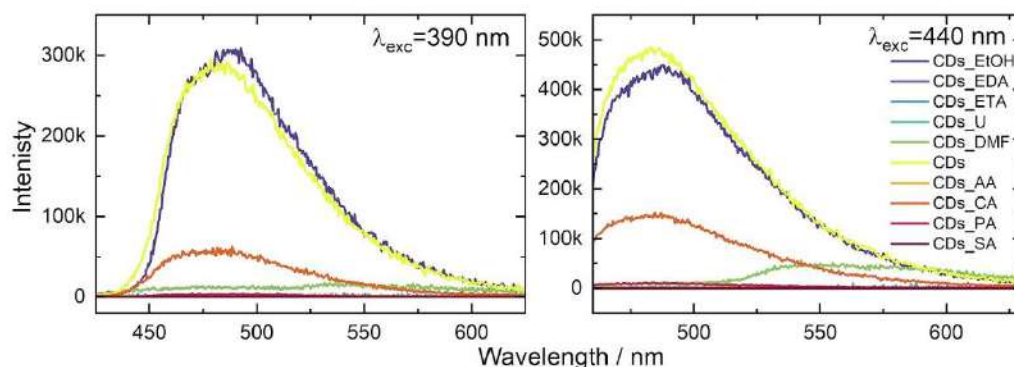


Fig. 5. Fluorescence emission spectra of carbon dots synthesized with different modifiers under selected excitation wavelengths, illustrating both excitation-dependent emission behavior and differences in emission intensity related to surface chemistry.

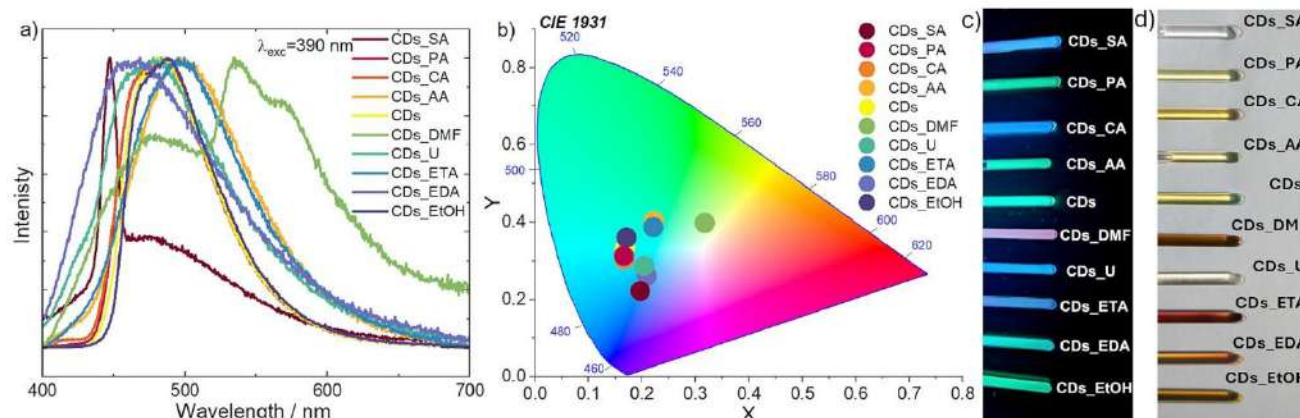


Fig. 6. A) normalized emission spectra of carbon dots without and with different modifiers under 390 nm excitation. Peak maximum comparison. b) CIE diagram of CDs without and with different modifiers under 390 nm excitation c) image showing the multicolor fluorescence of various CDs samples under a UV lamp ($\lambda_{\text{exc}} = 365$ nm) d) under sunlight.

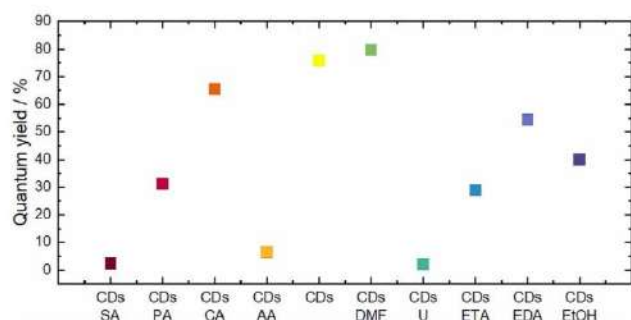


Fig. 7. The quantum yield of carbon dots with and without a modifier.

CDs_U showed an extended lifetime of 6.09 ns, likely due to the incorporation of nitrogen-containing groups (e.g., $-\text{NH}_2$, $-\text{CONH}_2$), which can introduce mid-gap states or stabilize excited states. Samples modified with CA, PA, DMF, and EtOH exhibited lifetimes comparable to the unmodified CDs (5.36–5.94 ns), indicating a moderate influence of these agents. Notably, CDs_ETA, modified with ethanolamine, displayed the shortest lifetime (3.38 ns), possibly due to the formation of surface states acting as efficient quenching centers or structural disorder enhancing non-radiative decay [29]. Three samples – CDs_U, CDs_EDA, and CDs_DMF- exhibited biexponential decay profiles with two distinct lifetime components, where the longer components (5.4–6.1 ns) were attributed to radiative recombination from passivated or graphitic core

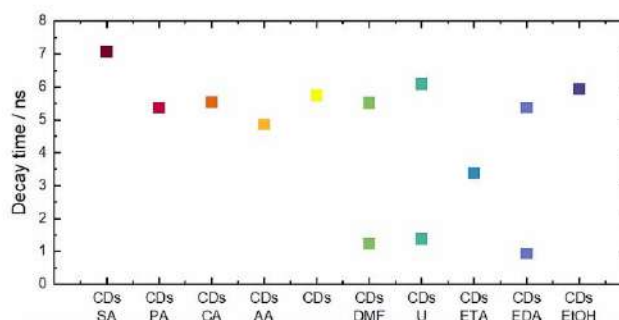


Fig. 8. Average fluorescence lifetimes of reference and modified carbon dots, illustrating the influence of surface functionalization on excited-state relaxation pathways.

states, while the shorter components (0.94–1.37 ns) likely originated from defect-related or surface-localized emissive states. These findings support a mechanism in which surface passivation, especially through functional groups containing sulfur or nitrogen, plays a critical role in modulating the lifetime by reducing surface trap-mediated relaxation [29]. Moreover, the presence of dual decay components reflects emission from multiple recombination centers, confirming the heterogeneity in surface and core states [37]. The varying polarities and electronic properties of the modifying reagents likely affect the distribution and density of emissive centers, contributing to the observed differences in

lifetime behavior.

A detailed analysis of fluorescence lifetimes measured at different excitation and emission wavelengths (Table 5) provides insight into the contribution of core- and surface-related emissive states in the studied carbon dots. For each excitation wavelength (257, 390, and 500 nm), the selected emission wavelengths represent emission originating predominantly from the carbon core, interfacial core-surface states, and surface functional groups, respectively [43]. The reference CDs exhibit nearly constant lifetimes (5.2–5.7 ns) across all excitation and emission wavelengths, indicating a dominant radiative recombination pathway with a relatively homogeneous distribution of emissive centers [44]. In contrast, CDs modified with acidic agents show pronounced wavelength-dependent behavior. CDs_{SA} display significantly prolonged lifetimes, reaching up to 12.11 ns under 257 nm excitation, which indicates strong stabilization of excited states by sulfur-related surface groups [45]. At lower excitation energies and longer emission wavelengths, a gradual lifetime shortening is observed, suggesting activation of non-radiative surface traps [46]. CDs_{PA} and CDs_{CA} exhibit moderately stable lifetimes (5–6 ns) in the core and interfacial emission regions, followed by a decrease at longer wavelengths, consistent with recombination via oxygen- and phosphorus-containing surface states [38]. CDs_{AA} show slightly extended lifetimes at intermediate emission wavelengths, indicating the presence of shallow emissive surface states [44]. Samples modified with nitrogen-containing agents exhibit markedly different decay dynamics. CDs_{DMF} consistently show the shortest lifetimes among all samples (typically 1–2 ns), indicating that charge-transfer processes dominate the excited-state relaxation and strongly enhance non-radiative decay [47]. In contrast, CDs_{ETA} exhibit intermediate lifetimes (3–5 ns), suggesting partial surface passivation combined with the presence of amine-related quenching centers [48]. CDs_{EDA} and CDs_U show comparable intermediate behavior, reflecting a balance between surface-state emission and non-radiative relaxation pathways [49]. CDs_{EtOH} present lifetime values like the reference CDs, indicating that hydroxyl-rich surface modification has a limited influence on excited-state dynamics and does not introduce deep trap states [50]. Overall, the lifetime data confirm that surface chemistry plays a decisive role in determining excited-state relaxation pathways in carbon dots. Acidic modifiers tend to stabilize excited states and prolong fluorescence lifetimes, whereas nitrogen-containing modifiers – particularly aprotic solvents such as DMF – promote charge-transfer processes and significantly shorten fluorescence lifetimes. These findings support a multi-emissive-center model involving carbon core states, interfacial states, and functional-group-related surface states [8,38].

It is important to note that extended fluorescence lifetime does not necessarily correlate with increased quantum yield. For instance, carbon dots modified with sulfuric or phosphoric acid exhibit prolonged excited-state lifetimes due to effective surface passivation; however, their quantum yields remain moderate because of competing non-radiative relaxation pathways associated with highly oxidized surface

groups. In contrast, DMF-modified carbon dots display exceptionally high quantum yield at low concentrations despite relatively short fluorescence lifetimes, indicating that fast radiative recombination through charge-transfer surface states dominates the emission process. These observations clearly demonstrate that fluorescence lifetime and quantum yield are governed by distinct aspects of surface chemistry and excited-state dynamics.

To facilitate direct comparison of the influence of different chemical modifiers on the structural and photophysical properties of carbon dots, a comprehensive correlation summary is provided in Table 6.

3.8. Mechanism

The photoluminescence behavior of synthesized carbon dots can be explained using a multi-emissive-center model, in which radiative recombination occurs through a combination of carbon core states, core-surface interfacial states, and states associated with surface functional groups [8,38]. The relative contribution of these pathways is strongly dependent on the chemical nature of the modifier introduced during hydrothermal synthesis.

3.9. Carbon dots modified with acidic agents

Carbon dots synthesized in the presence of acidic modifiers (e.g., sulfuric, phosphoric, citric, and acetic acids) are characterized by the presence of surface functional groups containing oxygen, sulfur, phosphorus, such as C=O, O–H, S=O, P=O groups. These groups introduce electron-withdrawing functionalities that promote the formation of STS located energetically below the LUMO of the sp^2 carbon core. In these systems, excitation occurs primarily in the $\pi-\pi^*$ states of the carbon core, followed by relaxation to shallow or deep STS associated with heteroatom-containing functional groups. Radiative recombination from these states leads to relatively broad emission bands with limited dependence on excitation. However, excessive oxidation or the formation of strong electron-withdrawing groups can also introduce non-radiative recombination channels, which explain the reduced quantum yield observed for some acid-modified samples, despite their longer lifetimes. Carbon dots synthesized in the presence of acid modifiers such as sulfuric and phosphoric acids exhibit surface functional groups, including S=O, P=O, and P–O groups, which act primarily as electron-withdrawing and passivating agents rather than as strong electronic dopants. These groups introduce STS that are energetically close to the internal emission states of the carbon core and do not significantly alter the effective energy separation between the ground state and the emission states. As a result, the photoluminescence of CDs_{SA} and CDs_{PA} is characterized by relatively stable emission energies accompanied by extended fluorescence lifetimes. This behavior indicates that the dominant effect of the sulfur- and phosphorus-containing groups is the suppression of non-radiative recombination pathways through surface passivation, rather than the formation of deep emissive surface

Table 5

Comparison of the lifetimes of excited states of carbon dots for different emission centers – core, interfacial core – surface states (CS), functional groups (FG).

Modifier		SA	PA	CA	AA	ref	DMF	ETA	EDA	U	EtOH
λ_{exc}											
257 nm	Core	4.74	5.84	4.41	4.55	5.63	1.95	3.49	2.91	1.81	5.2
	CS	7.34	6.17	4.82	5.46	5.65	1.72	4.31	3.52	2.51	5.33
	FG	12.11	6.41	9.84	7.14	5.71	6	5.42	3.97	3.15	5.48
390 nm	Core	5.63	5.72	4.88	4.36	5.25	1.19	3.8	3.06	3.39	5.17
	CS	6.01	5.73	5.47	5.77	5.44	1.29	3.74	2.35	3.8	5.33
	FG	5.62	5.9	6	7.56	5.46	2.37	3.57	2.35	3.73	5.47
500 nm	Core	3.62	5.74		5.53	5.35	1.22	2.1	4.45	3.96	4.67
	CS	3.31	4.9	4.92	5.53	4.48	1.23	1.74	4.86	2.72	3.69
	FG	2.97	3.82	3.92	4.83	3.36	2.38	1.36	4.58	2.31	2.58

Table 6

Correlation between chemical modifiers, surface functional groups, and photophysical properties of carbon dots.

Modifier	Dominant surface groups (FTIR / chemistry)	Emission behavior	QY trend	Lifetime trend	Dominant mechanism
CDs_SA	S=O, C=O, O-H	Dual-band emission with noticeable excitation-dependent spectral shifts	Low (<40%)	Longest (~7 ns)	Stabilized deep STS, non-radiative channels
CDs_PA	P-O, P-OH, C=O	Dual-band emission with weak excitation dependence and minor spectral shifts	Low moderate (<40%)	Extended (~6–7 ns)	Stabilized STS, surface passivation
CDs_CA	C=O, COO ⁻ , O-H	Broad emission with weak excitation dependent	High (~65%)	~5–6 ns	Surface passivation, STS
CDs_AA	C=O, COO ⁻	Dual-band emission under high-energy excitation, excitation dependent	Low (<40%)	~5–6 ns	Multiple surface emissive centers
CDs	O-H, C=O, sp ² C=C	Predominantly single-band emission with weak excitation dependence	High (~75%)	~5.7 ns (single-exponential)	Core + shallow surface states
CDs_DMF	C-N, N-O, N-H	Multi-band emission with moderate excitation dependence	Very high (up to ~80% at low concentration)	Short dominant component (~1–2 ns) with longer CT-related component (~6 ns)	Fast charge-transfer states
CDs_U	N-H, C=O, C-N	Dual-band emission with moderate excitation dependence	Low (<40%)	~6 ns (bi-exponential)	Surface states + charge transfer
CDs_ETA	C-N, N-H, O-H	Excitation-dependent emission with moderate red-shift	Low (<40%)	Shortest (~3.4 ns)	Non-radiative surface quenching
CDs_EDA	C-N, N-H	Excitation-dependent emission with pronounced red-shift under varying excitation wavelengths	Moderate (~54%)	~3–4 ns (bi-exponential)	Donor-induced surface states
CDs_EtOH	O-H, C-O	Single broad band with weak excitation dependence	Moderate (~40%)	~5.5 ns	Core states with shallow STS

states [42,43]. The appearance of narrow emission features superimposed on broader bands suggests the presence of well-defined, localized emission centers, likely associated with specific defect configurations or rigid surface complexes formed during synthesis. Although the lifetimes of the excited states are extended, the quantum yield remains moderate, indicating that radiative recombination competes with residual non-radiative relaxation channels introduced by the highly oxidized surface [46,50].

3.10. Carbon dots modified with basic and nitrogen reagents

Carbon dots modified with basic or nitrogen reagents (e.g., ethylenediamine, ethanolamine, urea, and DMF) exhibit fundamentally different emission mechanisms. Nitrogen-containing functional groups, such as -NH₂, -CONH₂, and C-N, introduce electron-donating states that strongly interact with the π -conjugated carbon core, leading to donor-acceptor and charge-transfer states [29,38,49]. Excitation-dependent photoluminescence is evident in these samples, reflecting the presence of multiple emission centers with varying energy depths. High-energy excitation populates core-bound states, while lower-energy excitation selectively affects deeper surface or charge-transfer states, leading to gradual redshifts in the emission. This behavior is particularly evident in CDs_EDA, CDs_ETA, and CDs_DMF, where multiple emission bands and biexponential decay profiles confirm the coexistence of several independent recombination pathways. DMF-modified carbon dots represent an extreme case in which strong charge-transfer interactions dominate the excited-state dynamics. Although these systems exhibit very high quantum yields at low concentrations, their short fluorescence lifetimes indicate that radiative recombination occurs via fast surface channels rather than through the surface.

3.11. General mechanism

In general, acidic modifiers modulate photoluminescence primarily by stabilizing surface trap states and influencing surface passivation, whereas basic modifiers introduce donor states and charge-transfer pathways that enhance excitation-dependent emission and spectral tunability. The balance between radiative and nonradiative relaxation pathways is therefore governed by the type, density, and electronic nature of the surface functional groups, enabling precise control over emission color, quantum yield and excited state lifetime.

4. Conclusion

Based on the research conducted, it can be concluded that the application of different chemical modifiers has a significant impact on the surface composition and optical properties of carbon dots (CDs). Both acidic and basic modifiers introduce distinct functional groups, as confirmed by FTIR spectroscopy, each sample exhibited unique vibrational bands characteristic of groups such as C=O, S=O, P=O, and N-H. These surface modifications directly influence the emission mechanisms, particularly in samples modified with nitrogen-containing compounds (e.g., EDA, ETA, U), which showed pronounced excitation-dependent photoluminescence and multiphase emission profiles. CDs within the alkaline/aprotic system, such as CDs_DMF, achieve the highest QY, exceeding 80%. Their primary advantage lies in the introduction of donor states that minimize non-radiative losses. Conversely, in the acidic system, CDs_SA proved to be the superior choice for applications requiring high excited-state stability, as they exhibited the most prolonged lifetimes (7.07 ns). The absorption spectra revealed characteristic π - π^* and n - π^* transitions, whose position and intensity varied with the type of modifier used, indicating that surface chemistry strongly affects the electronic structure of CDs. Notably, modifiers such as DMF and CA significantly enhanced the photoluminescence performance, achieving QY above 70% and even exceeding 80% under optimized conditions. An inverse relationship was observed between carbon dot concentration and QY-dilution led to increased emission efficiency, which is particularly important for applications in bioimaging and optical sensing, where high sensitivity is required. Fluorescence lifetime measurements confirmed that different modifiers introduce diverse relaxation pathways. Samples like CDs_SA and CDs_U exhibited extended lifetimes, suggesting effective surface passivation and reduced non-radiative losses, while others, such as CDs_ETA, showed shortened lifetimes indicative of enhanced quenching. In several cases, biexponential decay behavior was observed, pointing to the coexistence of multiple emissive centers located both within the core and on the surface of the nanoparticles. Importantly, the results show that acidic modifiers predominantly stabilize STS and extend excited state lifetimes, whereas basic and nitrogen-containing modifiers introduce donor and charge-transfer states that enhance excitation-dependent emission and spectral tuning capabilities. This clear distinction provides a practical strategy for the rational design of carbon dots with tailored photophysical properties. The ability to precisely control emission color, QY,

and lifetime through simple chemical modification makes these materials particularly attractive for advanced applications in fluorescence sensing, bioimaging, optoelectronics, and hybrid photonic systems. Overall, the results clearly demonstrate that careful selection of surface modifiers enables precise tuning of the optical properties and structure of carbon dots, making them highly promising materials for applications in photonics, bioimaging, catalysis, and as luminescent markers in chemical and biological analyses.

CRedit authorship contribution statement

Daniela Kujawa: Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Robert Tomala:** Writing – review & editing, Resources, Project administration, Funding acquisition. **Paweł Gluchowski:** Writing – review & editing, Supervision, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2026.166772>.

Data availability

I have shared the link to my data at <https://doi.org/10.5281/zenodo.18436183>

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Supplementary information

The influence of modifiers on the luminescent properties of carbon dots

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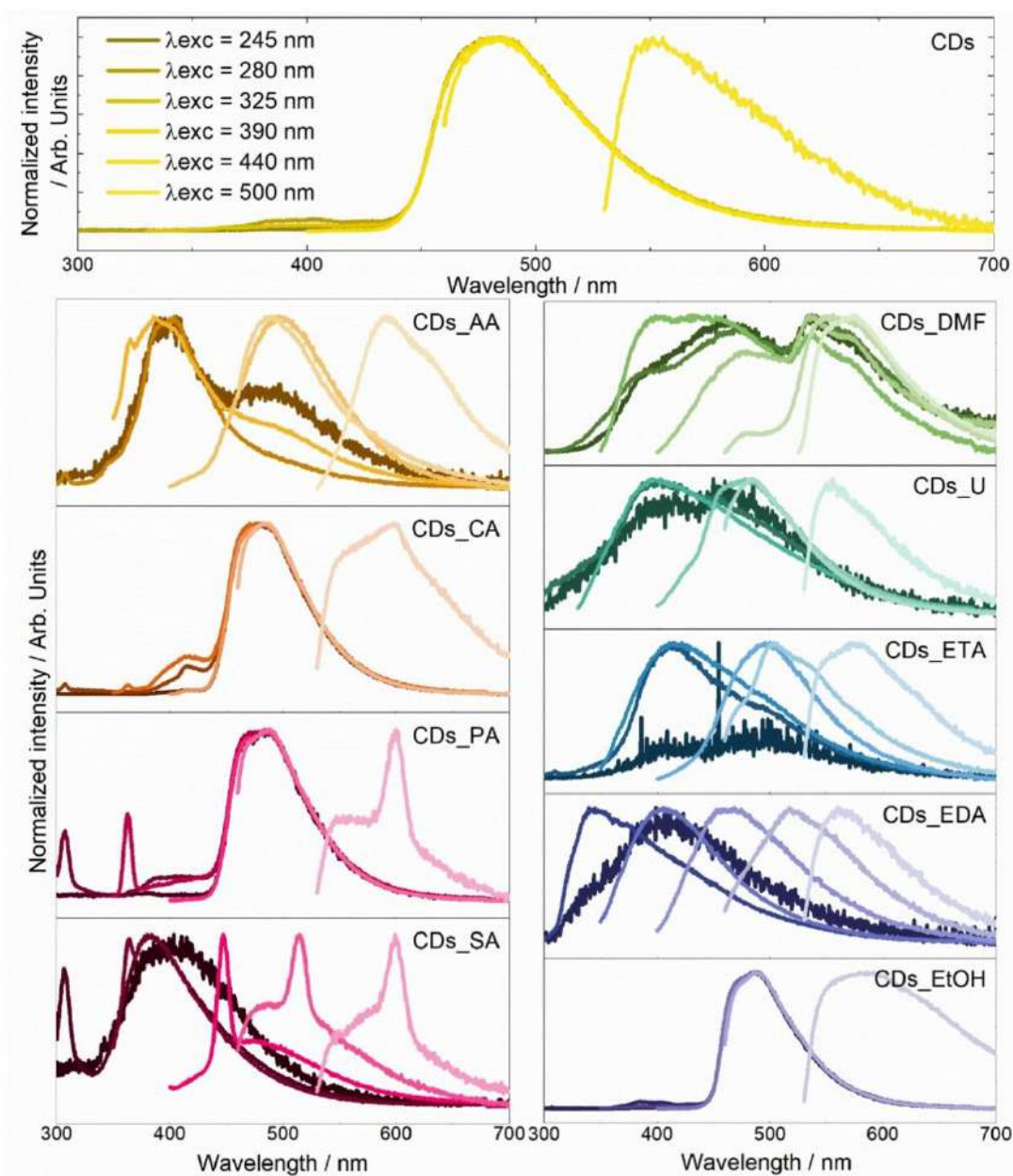


Fig S1. Normalized emission spectra of carbon dots a) without and with b) acid and b) alkaline modifiers. Peak maximum comparison

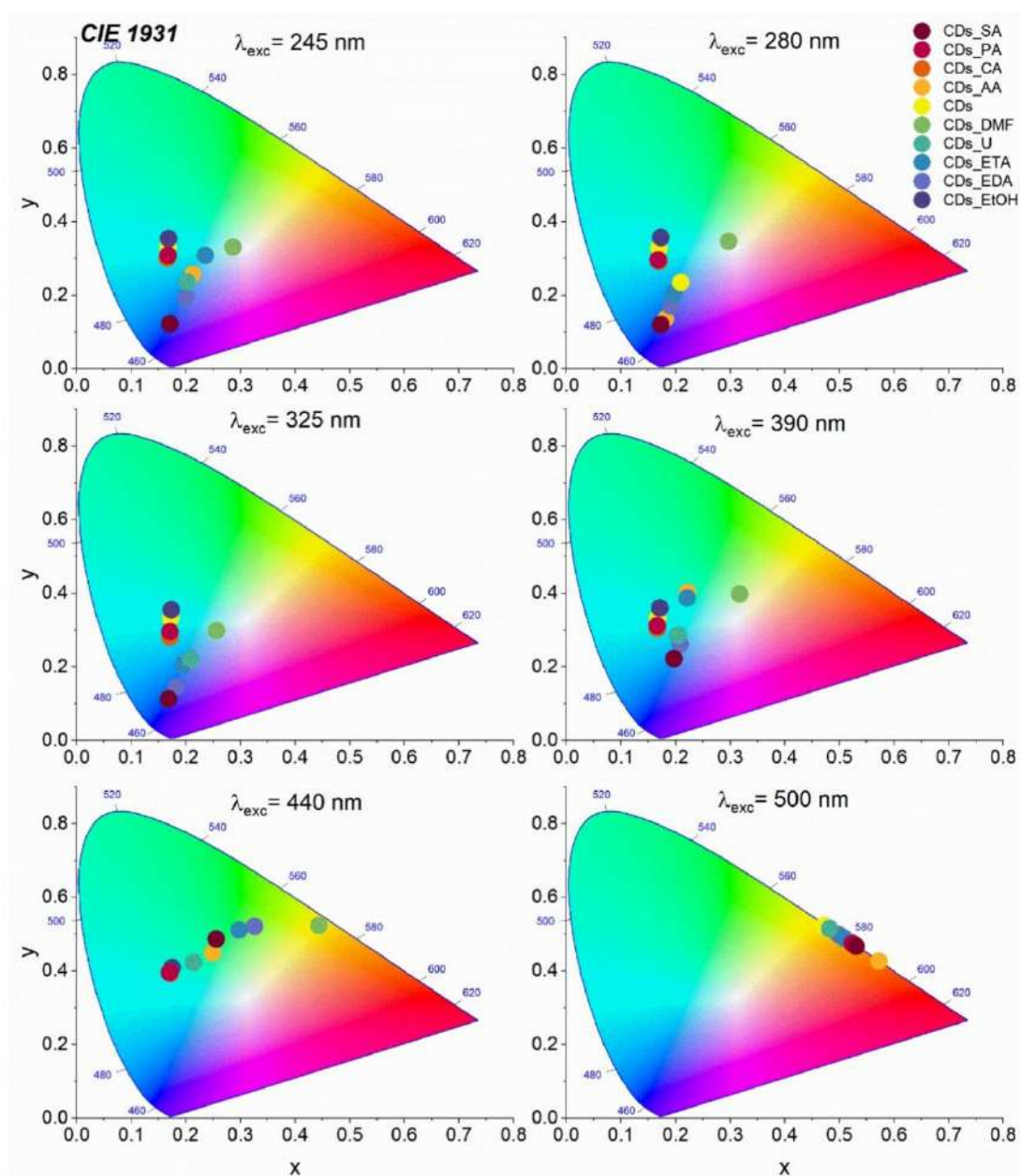


Fig S2. CIE diagram of carbon dots without and with modifiers under different excitation wavelength

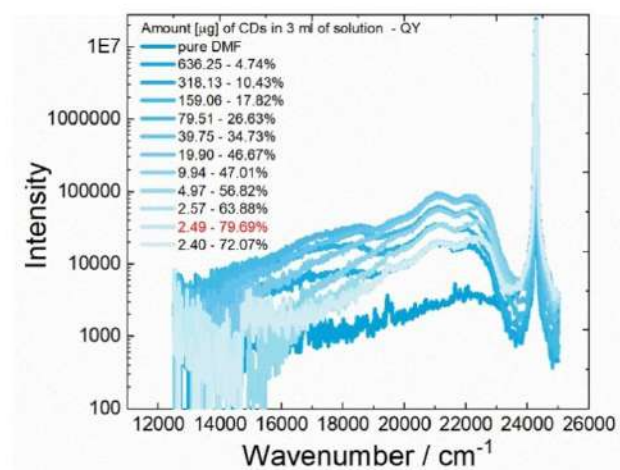


Fig S3. Comparison of quantum yields of CD_DMF with different concentrations.

8.1.2. Development of fast and ecological methods for obtaining carbon dots with high spectral sensitivity to pH changes and the presence of hydroxyl groups (published)

Publication P2 represents an extension of research on CDs, shifting the focus toward understanding their dynamic surface nature and molecular interactions with the environment. The primary objective of this study was to investigate how specific functional groups on nanostructure surfaces respond to changes in their immediate chemical environment. This work demonstrates that the optical properties of CDs depend on the surface protonation state and hydrogen bonding interactions. Consequently, it was proven that these materials can serve as very sensitive environmental probes, capable of monitoring subtle physicochemical changes.

Within the framework of this publication, an efficient and low-cost method for obtaining CDs was developed via pyrolysis, utilizing non-toxic precursors: citric acid and urea, with the addition of sodium hydroxide. The process was conducted at 260°C for 5 hours, allowing for controlled carbonization of the mixture. The synthesis resulted in nanostructures with a unique architecture: a partially crystalline graphene-like core surrounded by a dense network of polymeric functional groups. Structural XRD analyses confirmed the presence of the characteristic graphene (002) band and additional crystalline phases. Importantly, these phases disappear upon dissolution in alcohols, providing direct evidence of the deep penetration of the dot structure by solvent molecules.

A key research achievement was the demonstration of a continuous change in absorption and emissions across a broad pH range (1–14) (Fig. 7). It was observed that increasing environmental alkalinity induces an increase in absorption intensity and a blue shift and an increase in luminescence intensity. This mechanism is closely correlated with the deprotonation state of carboxyl and hydroxyl groups on the dot surface, which modifies the electronic environment of the chromophores and alters the energy levels of the excited states.

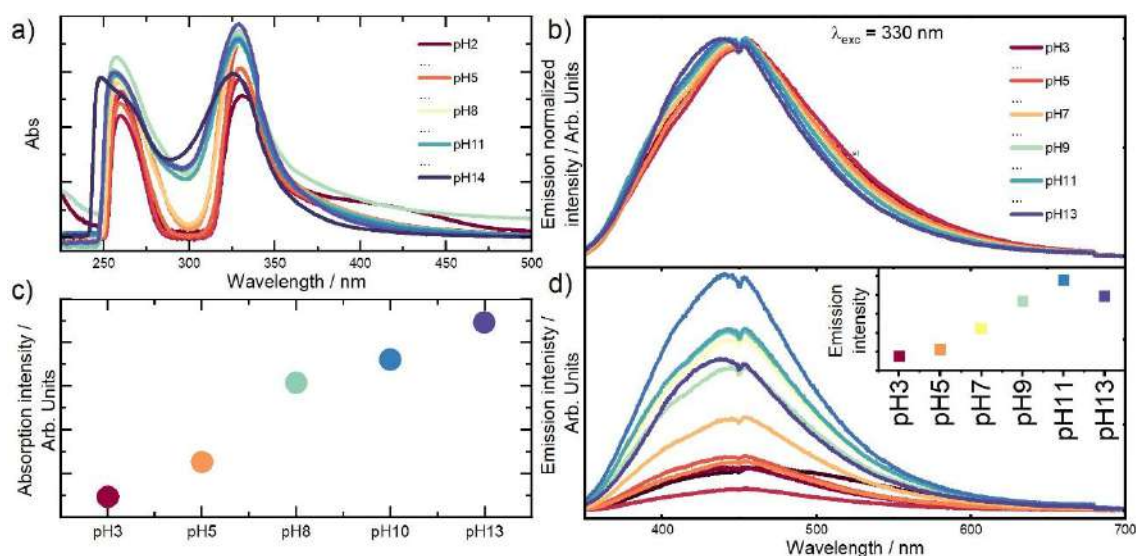


Figure 7. Absorption spectra (a) and a graphical presentation of the relationship between absorption intensity and pH (c) for carbon dots. Emission spectra under 330 nm excitation for carbon dots in solvents with different pH. Reprinted with permission from [155]

Simultaneously, the article describes a unique sensitivity of CDs to the presence of hydroxyl groups in organic solvents (Fig. 8). In contrast to pH solutions, redshift was observed in alcoholic media. It was shown that the intensity of the absorption band at 330 nm increases proportionally to the number of available -OH groups in the solvent (e.g., glycerin or PEG), resulting from the stabilization of electronic states through hydrogen bonding and changes in the probability of $n \rightarrow \pi^*$ transitions.

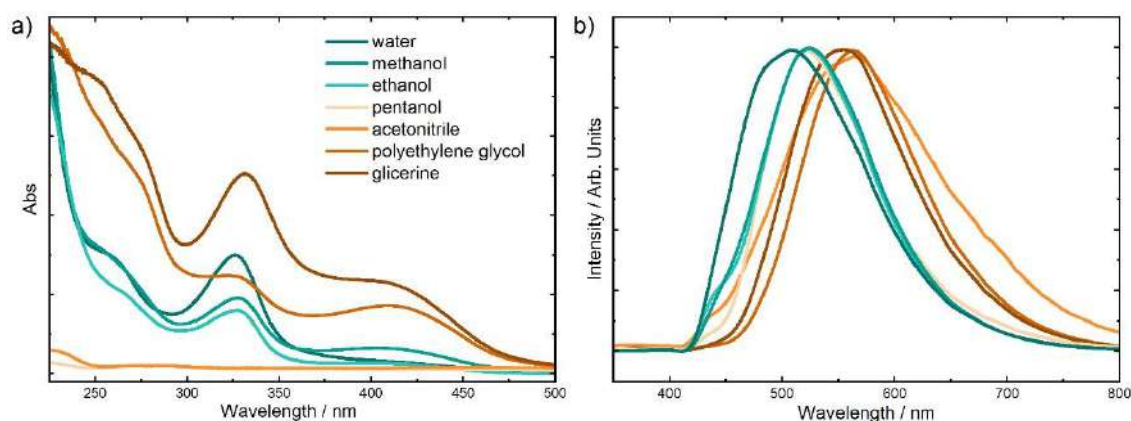


Figure 8. Absorption (a) and emission (b) spectra of carbon dots in different organic solvents. Reprinted with permission from [155].

An innovative aspect of the publication was the use of FTIR to monitor the real time surface reorganization of CDs during solvent evaporation. These measurements revealed

that methanol induces faster structural changes than ethanol, due to its smaller molecular size and its ability to penetrate CDs aggregate more deeply. The emergence of new vibrational bands during this process indicates a dynamic reconfiguration of the polymer chains and the hydrogen bond network on the sensor surface (Fig. 9).

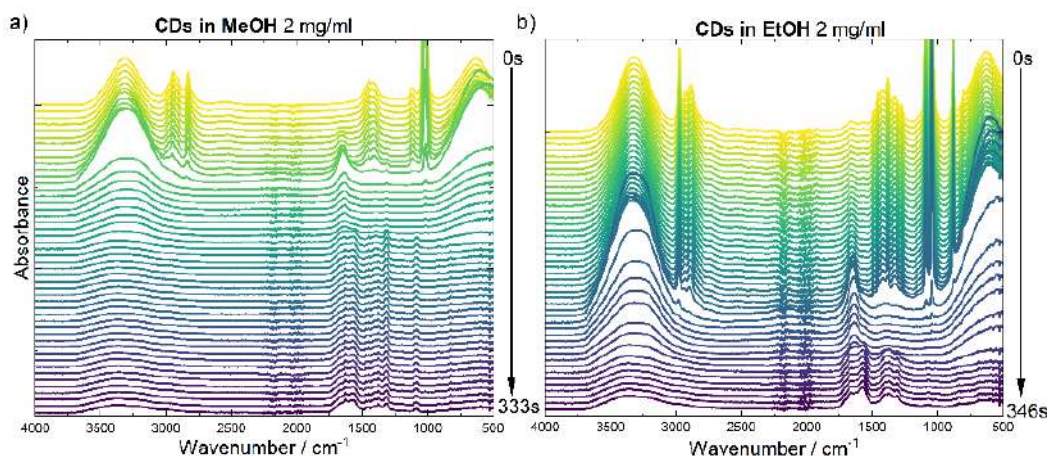


Figure 9. Time - evolution of IR spectra collected for CDs in methanol and ethanol.

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The most important conclusion of this work is the demonstration that CDs are dynamic systems whose optical properties directly reflect the chemical state of their surfaces. The results also showed that by manipulating hydrogen bonds and the protonation state, one can precisely control the material's spectral response.

The ability to interact so strongly with the molecular environment, demonstrated in this publication, suggests that CDs can not only passively detect environmental changes but also may enable interactions relevant to energy transfer. This property was utilized in the subsequent stage of research, where these dots served as sensitizers in hybrid photocatalytic systems designed to degrade organic pollutants.

Author contribution to the publication P2

conceptualization, carrying out chemical synthesis, selecting reagents and performing preliminary tests of their effect on the optical properties of materials, preparing materials for structural and morphological studies, performing spectroscopic measurements, analyzing the results of spectroscopic, XRD and TEM measurements and preliminary analysis of IR results, data processing and preparing their graphic visualization, planning

the structure of the manuscript, preparing the initial and final versions of the manuscript, preparing responses to reviewers, archiving data after preparing the final article



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A rapid, green and cost-effective synthesis of pH- and hydroxyl group sensitive carbon dots for sensing applications†

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A rapid, green, and cost-effective method for synthesizing carbon dots (CDs) was developed using non-toxic, low-cost precursors via a simple combustion process. The resulting CDs exhibit strong and tunable photoluminescence, high photostability, and excellent dispersibility in aqueous media. Structural and spectroscopic analyses confirmed the presence of a partially crystalline graphene-like carbon core surrounded by polymeric surface functionalities. The synthesized CDs display dual environmental sensitivity: continuous emission shifts were observed across a broad pH range (1–14), as well as distinct spectral responses depending on the presence and nature of hydroxyl groups in organic solvents. Infrared (IR) spectroscopy revealed dynamic surface interactions and structural transformations during solvent evaporation, particularly in methanol and ethanol. Methanol induces faster changes in the IR spectrum than ethanol. UV-Vis absorption and photoluminescence spectroscopy demonstrated that the emission wavelength and intensity of the CDs vary significantly depending on solvent polarity, hydroxyl group content, and carbon chain length. In aqueous media, increasing pH induced a blue shift and enhanced emission intensity, while in alcohols, red shifts were observed. The unique sensitivity of the CDs to both pH and hydroxyl-rich environments highlights their potential utility as label-free, real-time sensors. Given their biocompatibility, photostability, and solvent-responsiveness, the synthesized CDs offer promising applications in biomedical diagnostics, food safety (e.g., methanol detection), and environmental monitoring. The study demonstrates how a sustainable and scalable synthetic route can yield multifunctional carbon-based nanomaterials with advanced sensory properties.

Introduction

Carbon dots (CDs) are a class of nanomaterials composed of a carbon core with a graphene-like structure, typically functionalized

with various chemical groups on their surface. These materials exhibit extensive luminescent properties, including narrowband and/or broadband emission across the entire visible spectrum. Their bandgap energy can be tuned, and excitation wavelengths can be modulated by controlling the particle size and surface group types. Moreover, CDs are capable of exhibiting both fluorescence and phosphorescence under specific conditions.^{1,2} Due to their tunable photophysical behavior and ease of surface modification, CDs have recently gained significant attention in nanotechnology and optoelectronics, emerging as versatile materials for bioimaging, sensing, and light-emitting devices.^{3–6} Their sensitivity to minor environmental changes makes them excellent candidates for use in sensing applications. Prior studies have demonstrated that CDs can serve as effective probes for detecting a wide variety of analytes, including heavy metal ions, dopamine, glucose, and nitroaromatic compounds.^{7–9} Furthermore, CDs have been successfully implemented as pH sensors, which are crucial in fields such as biomedical diagnostics (e.g., monitoring disease-associated pH variations), food quality control, and drug delivery systems sensitive to microenvironmental pH changes.^{10–12} However, many of these sensors are limited by their narrow operational pH range and typically rely on changes in fluorescence intensity rather than wavelength shifts. Additionally, most reported syntheses involve the use of complex and potentially hazardous organic reagents such as amines, which limits their practical and sustainable scalability.¹³ CDs have also shown promise as fluorescent probes for detecting alcohols, particularly methanol (MeOH) and ethanol (EtOH).^{7,14} Prior research has mainly focused on detecting these substances in solution, typically through fluorescence quenching mechanisms. Notably, a recent study demonstrated the use of nitrogen-doped oxidized carbon dots capable of differentiating between methanol and ethanol based on the magnitude of fluorescence quenching. In that study, the presence of 1% methanol in distilled water resulted in a reduction of fluorescence intensity by more than 90%, whereas ethanol concentrations as high as 70% induced less than a 20% change in signal.¹⁵

In contrast to conventional CDs, which are often synthesized using complex, multi-step procedures involving toxic or

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expensive reagents such as amines, the carbon dots developed in this study were produced *via* a simple, low-cost combustion method using safe and readily available precursors such as citric acid and urea.¹⁶ This greener and more scalable approach eliminates the need for hazardous chemicals while maintaining excellent optical properties. The resulting CDs exhibit solvent-dependent spectral behavior, including distinct emission wavelength shifts in various alcohols and organic solvents.^{17,18} Notably, they exhibit continuous and reversible fluorescence wavelength shifts across a broad pH range—unlike many conventional systems that rely solely on intensity changes within narrow operational windows.¹⁹ Thanks to their biocompatibility, photostability, and high quantum yield, these materials show great potential for applications in diverse sectors, including medical diagnostics and the food industry.

Experimental

Materials and synthesis of samples

Carbon dots were synthesized by mixing citric acid (CA), urea (U), and sodium hydroxide in a ratio of 1:1:0.4 in an aqueous solution. The resulting solution was then subjected to pyrolysis at 260 °C for 5 h.

Equipment

X-ray diffraction (XRD) measurements were performed at room temperature using a PANalytical X'Pert PRO diffractometer (Malvern Panalytical, UK) equipped with Cu K α_1 radiation ($\lambda = 1.5406$ Å). Data were collected over a 2θ range of 10–80°, with a step size of 0.03°.

Transmission electron microscopy (TEM) analyses were conducted using a Philips CM-20 SuperTwin microscope operating at an accelerating voltage of 160 kV.

The IR-ATR spectra of powders and suspensions in the 4000–500 cm⁻¹ range were measured using a Nicolet iS50 FTIR spectrometer with a built-in ATR module with a diamond crystal; the spectral resolution was set to 2 cm⁻¹. The ground powders were loaded directly on the crystal, pressed down, and the spectra were collected. To measure suspensions in water, methanol, ethanol, 1-pentanol, ethylene glycol, glycerol, and acetonitrile, 100 μ l of liquid was placed on the ATR crystal, and no pressure was applied.

UV, Vis, and NIR absorption spectra were recorded at room temperature using a Varian Model 5E spectrophotometer. The spectrophotometer covered a wavelength range of 200–800 nm and had a spectral bandwidth set to 0.1 nm.

Photoluminescence (PL) emission spectra were obtained using an Edinburgh Instruments FLS980 fluorescence spectrometer (Livingston, UK). The system was equipped with a 450 W xenon lamp as the excitation source, monochromators configured in a Czerny–Turner arrangement with 1800 lines per mm holographic gratings and 300 mm focal length, and a Hamamatsu R928P photomultiplier tube (side window configuration) as the detector.

Time-resolved emission measurements were carried out using an Ocean HDX high-resolution spectrometer (Ocean Optics, USA) and a 330 nm excitation LED source. The Ocean HDX spectrometer features a compact optical bench design with high thermal stability, 200 to 1100 nm spectral coverage, enhanced signal-to-noise performance, and fast acquisition times, making it ideal for kinetic studies.

Results and discussion

To investigate the structural ordering and crystalline features of the synthesized carbon dots, XRD analysis was performed. The XRD pattern (Fig. 1(a)–(c)) reveals that the studied CDs exhibit a partially amorphous structure with crystalline components. The amorphous character is evidenced by broad diffraction peaks, including those centered at approximately 18° and 26° 2θ . The first broad feature (*ca.* 18° 2θ) can be attributed to an amorphous polymeric phase, indicating the formation of polymeric networks during the synthesis. Such structures are consistent with previous reports in which citric acid and urea undergo thermal condensation into polymer-like matrices.^{20,21} Similar syntheses have been shown to result in crystalline materials under different conditions.^{22,23} The current synthesis route yields disordered polymers. The second broad peak at *ca.* 26° 2θ corresponds to the (002) reflection of the graphene structure, indicating that the core of the CDs is composed of stacked graphene layers. Sun *et al.* described a comparable behavior²⁴ during incorporation of sodium hydroxide (NaOH) into a polyvinyl alcohol (PVA) matrix. Their XRD analysis has shown the transformation of hydroxyl (–OH) groups into sodium alkoxide (–ONa), resulting in narrow diffraction peaks. This has been interpreted as an improvement in the purity and order of the polymeric system. In our case, the presence of narrow peaks may similarly indicate partial crystallization or the presence of residual inorganic phases on the CDs surface. In this case, the CDs are composed of a carbon core with a graphene structure, which has long polymer chains on its surface, consisting of NH–CO–NH–CO–CH₂–C(OH)(COONa)–CH₂–CO_{*n*}.

TEM imaging was conducted to examine the morphology, size, and aggregation state of the carbon dots at the nanoscale. The morphology of the CDs was studied by TEM imaging at different magnifications (Fig. 1(d)–(f)). Image (d) reveals an irregular and rounded aggregate structure with a distinctly irregular, porous surface covered with numerous protrusions with a morphology resembling finger-like or spiky formations. These protrusions spread radially from the surface, which may indicate nanoparticle's directional growth or local agglomeration during the synthesis process. Image (e) shows the surface texture in more detail, which is highly inhomogeneous and contains both amorphous regions and fine porous structures. We can also observe the structures (in red circles) that are less than 10 nm in size, which are carbon dots. In image (f), thin, layered flakes with irregular contours were observed, probably fragments of graphite-like structures or thin layers of carbon,

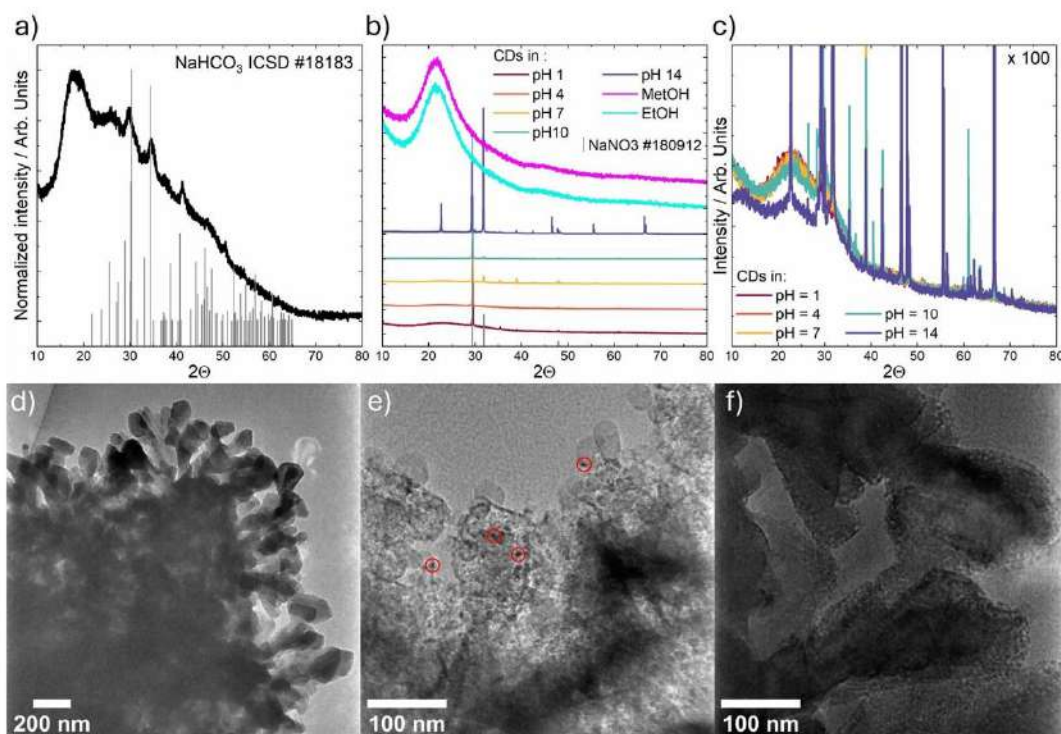


Fig. 1 XRD diffractogram for (a) pure CDs, (b), (c) CDs in solutions with different pH and in alcohols, (d)–(f) TEM images of pure CDs for different magnetization, red circle show carbon dots.

which partially cover the surface. The presence of such layers may indicate local rearrangement of carbon structures during carbonization.

Structural changes were also observed after redispersing the CDs in various solvents, including methanol, ethanol, and aqueous solutions of different pH (Fig. 1(b) and (c)). After dissolving in alcohols, the CDs lose their crystallinity, and only the graphene band with a maximum at 22° 2θ remains. Alcohols, particularly those with smaller molecular sizes such as methanol and ethanol, may penetrate the porous and polymeric surface functionalities of the CDs more effectively than water. This penetration could disrupt the weaker intermolecular forces maintaining the partial crystallinity, leading to a more disordered, amorphous state. The hydroxyl groups of the alcohols might form hydrogen bonds with the surface functional groups of the CDs, competing with and breaking existing hydrogen bonds within the CD structure, thereby reducing its ordered arrangement. The graphene band is also visible in suspensions where the CDs were dissolved in solutions with different pH, levels, but a dominant crystalline structure can be observed. Peaks formed after dissolving the dots in a solvent solution of pH = 14 can be assigned to the sodium nitrate structure (NaNO_3 ICSD #180912), which is not a material with luminescent properties.

IR spectroscopy was employed to identify the functional groups present on the surface of CDs and to investigate their interaction with various solvents over time. To understand the interactions of

CDs with different solvents, IR measurements were performed for 2 mg mL^{-1} of CDs in water, MeOH, and EtOH. The measurements were performed as a function of time. The spectrum of the water suspension exhibits a broad doublet band at approximately 3300 cm^{-1} , characteristic of OH stretching bonds, and a band at approximately 1650 cm^{-1} attributed to the bending vibrations of water molecules.^{25,26} (Fig. S1, ESI†). No characteristic bands from CDs can be seen (see the reference spectrum in Fig. S2, ESI†), as they are covered by strong absorption bands from water. In addition, the spectrum does not change qualitatively after approx. 30 min due to the slow evaporation of water at room temperature (RT).

IR spectra of CDs suspended in MeOH and EtOH were measured at intervals of a few seconds from 0 to approximately 6 minutes (Fig. 2(a) and (b)). The qualitative changes observed for the two liquid phases are very similar, but for MeOH they occur faster. The initial spectrum is dominated by the characteristic bands originating from methanol.²⁷ Over time, bands of MeOH gradually decrease and become barely visible at about 90 s. This process is accompanied by an ongoing increase in the intensity of a new band observed after 25 s, near 1660 cm^{-1} , and broadening of the contour near 3300 cm^{-1} . The spectrum of the new phase remains dominant until about 125 s, where it begins to partially disappear with the simultaneous appearance of bands at 3370 , 1630 , 1574 , 1472 , 1449 , 1400 , 1376 , 1315 , 1192 , 1086 , 917 , and 824 cm^{-1} . Analysis of the spectra allowed us to conclude that fast evaporation of MeOH causes the increased water concentration in the suspension coming from

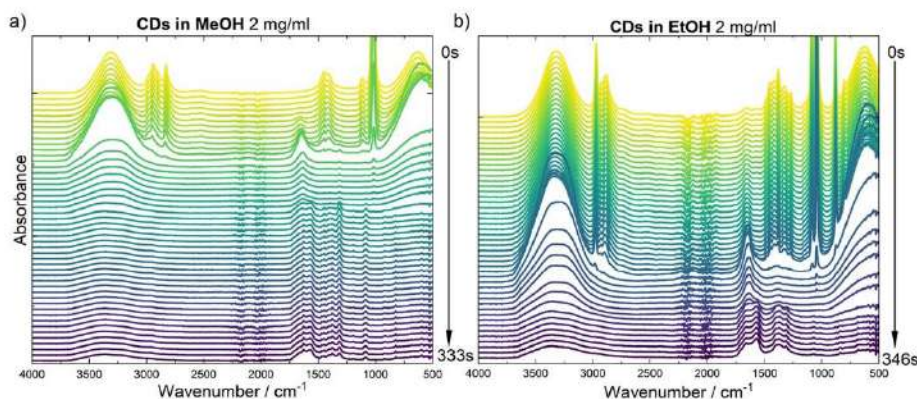


Fig. 2 (a) The time evolution of IR spectra collected for a 2 mg ml⁻¹ suspension of CDs in MeOH. (b) The time evolution of IR spectra collected for a 2 mg ml⁻¹ suspension of CDs in EtOH.

the solvent, sample, and/or air. Next, the water evaporates, revealing a spectrum of residues consisting of bands characteristic of CDs (Fig. S3, ESI†) and additional bands from washed-out citric acid and urea residues to the surface (see reference spectra in Fig. S4, ESI†). The observed changes in IR spectra during solvent evaporation (methanol and ethanol) likely reflect the dynamic reorganization of the CD surface. As the volatile alcohol evaporates, the concentration of water (from the environment or residual in the sample) increases, resulting in changes to the hydrogen bonding network surrounding the CDs. The appearance of a new band at ~ 1660 cm⁻¹ and the broadening around ~ 3300 cm⁻¹ could signify changes in the local environment of carbonyl (C=O) and hydroxyl (O-H) groups on the CD surface, possibly due to altered hydrogen bonding patterns or even conformational changes in the polymeric surface functionalities as the solvent environment changes. The faster changes in methanol compared to ethanol may be due to methanol's smaller molecular size, which allows for more rapid penetration into the CD aggregates and faster evaporation, thereby accelerating the surface restructuring processes. The "washing out" of citric acid and urea residues may be a consequence of the changing solvent polarity and solubility properties during evaporation, leading to their reprecipitation or aggregation on the surface as the more polar solvents (water, then residual alcohols) evaporate. Fig. 2(b) demonstrates the results of the corresponding experiment conducted in EtOH. Characteristic bands of EtOH dominate the recorded spectra until 226 s, after which the spectrum of water becomes dominant. After 263 s, the traces of ethanol are no longer detectable. The spectrum of residual CDs is dominant after 293 s (see Fig. S3, ESI†).

Fig. S3 (ESI†) compares the ATR spectra of CDs exposed to moisture and after the experiments when suspended in MeOH and EtOH. All spectra exhibit a broad contour above 3000 cm⁻¹, which is attributed to the stretching vibrations of OH groups, including those in water. These bands have two clear components, suggesting at least two types of OH groups in the CDs sample. The weak bands between 2800 and 3000 cm⁻¹ are characteristic of stretching vibrations of aliphatic CH₂ and CH₃

groups that may come from the traces of citric acid or solvents. Bands between 1555 and 1710 cm⁻¹ are due to the C=O and C=C stretching vibrations. The IR bands in the range of 1307–1472 cm⁻¹ are most likely related to bending (scissoring) vibrations of CH₂ and CH₃ groups and stretching vibrations of the carbon rings or aliphatic moieties. The weak bands between 1048 and 1070 cm⁻¹ originate from the C–O stretching vibrations. Among the bands located below, the one observed at 835 cm⁻¹ is assigned to ring vibrations, including C–C stretching or CCC bending. Two bands at 776 and 700 cm⁻¹ originate from bending vibrations of COO. The wide and intense bands below 600 cm⁻¹ are associated with torsional movements of hydroxyl groups.²⁸

Qualitatively, the spectra of CDs exposed to moisture and those of CDs after using EtOH are similar, except for the band at 774 cm⁻¹, observed only for the reference sample, and the change in intensity of bands corresponding to C–O stretching. This is the effect of modifying carboxyl groups on the surface after the experiment with EtOH. According to the literature data, this region is susceptible to the coordination of carboxyl group and/or its involvement in the formation of hydrogen bonds.^{29,30} In contrast to the EtOH experiment, the final spectrum of the CDs suspended in MeOH has additional bands and exhibits changes in relative intensity. A further band at 1629 cm⁻¹ may be assigned to the presence of other C=O groups and bending vibrations of NH₂ moieties, which can come from the urea as an impurity. Changes in relative intensity above 3000 cm⁻¹ support the presence of amino groups, because bands coming from OH and NH stretching overlap in this range. The CN stretching for urea is expected between 1452 and 1468 cm⁻¹, therefore, the band at 1472 cm⁻¹ was assigned to this vibration.³¹ According to the literature data, an additional band at 1193 cm⁻¹ can be attributed to the rocking vibration of NH₂ groups.³¹ The differences below 1100 cm⁻¹ originate from the differences within carboxyl groups. In conclusion, the amounts of impurities are significantly lower after the experiment with EtOH, which is reasonable due to the larger size of the EtOH molecule and its lower penetration capacity in the aggregates of CDs. The crystallization of urea and/or citric acid derivatives in EtOH is worse on the ATR crystal,

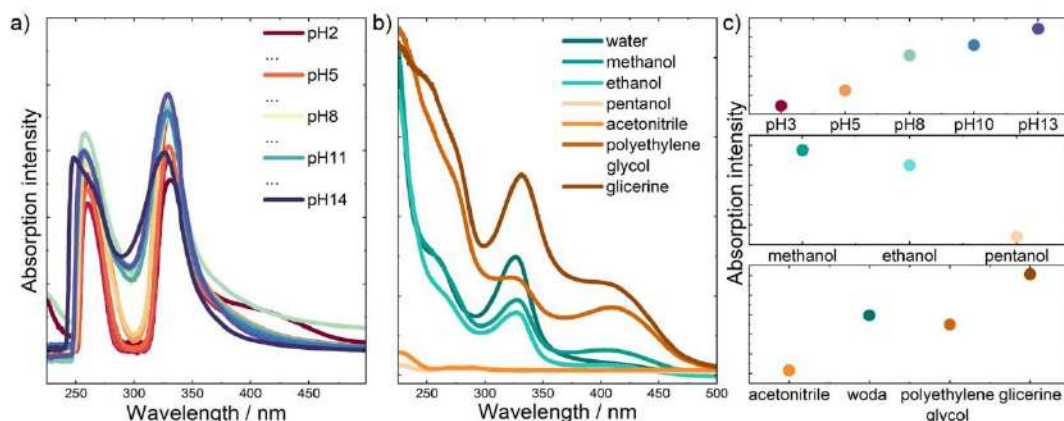


Fig. 3 Absorption spectra of CDs in (a) solvents with different pH and (b) with organic solvents, (c) Absorption intensity at 330 nm as a function of solution type: (top) solutions with varying pH, (middle) alcohols with different chain lengths, (bottom) solutions differing in OH group content and presence of lone electron pairs.

and the contribution of amorphous phases is higher than in MeOH. CDs were suspended in solvents such as 1-pentanol, glycerol, ethylene glycol, and acetonitrile. Only the IR bands associated with solvent molecules and/or impurities are visible for these media.

To understand the influence of pH on carbon dots, they were suspended in solutions with different pH, ranging from 1 to 14. The solutions were prepared by mixing appropriate amounts of nitric acid (HNO_3) with NaOH in water. The ATR spectra of pure solvents with different pH are presented in Fig. S5a (ESI[†]). The spectrum is composed of characteristic bands observed for water molecules (see Fig. S1, ESI[†]), *i.e.*, a doublet with a maximum at 3360 cm^{-1} (OH stretching) and a band at 1640 cm^{-1} (OH bending). Apart from these bands, a new doublet appears at 1386 and 1348 cm^{-1} , and a weak band is observed at approximately 1050 cm^{-1} . The intensity of the doublet increases with decreasing pH value; thus, it was assigned to the stretching vibrations of the NO_3^- ions.³² The weaker band is present only in the 1–7 pH range; therefore, it probably originates from the H_3O^+ ions. Furthermore, the shape of the broad contour at 3360 cm^{-1} changes with rising pH value, which is attributed to various $\text{H}_3\text{O}^+/\text{OH}^-$ ion concentration ratios.

The addition of CDs (2 mg ml^{-1}) to the pH-dependent solutions causes weak changes in the spectra, including the appearance of a band at 1570 cm^{-1} and four overlapped bands at 1388 , 1356 , 1311 , and 1257 cm^{-1} , which correspond well with bands of CDs (Fig. S2, ESI[†]). Interestingly, for suspension in pure water (Fig. S1, ESI[†]), the CDs' spectral features were not visible. It probably means that the higher ionic strength of the solution results in more efficient sediment suspension.

UV-Vis absorption spectroscopy was used to assess the optical absorption properties of CDs in various solvents and pH environments, which are critical for understanding solvent-dependent behavior. Absorption spectra were measured for three cases: (1) pH-buffered solutions compared to water, (2) pH-buffered solutions with suspended CDs compared to water (Fig. S6, ESI[†]), and (3) pH solutions with suspended CDs

compared to the corresponding pH solutions without CDs. The third comparison isolates the absorption attributable solely to the carbon dots (Fig. 3(a)). The pH base solution exhibits a broad absorption band with a maximum at approximately 300 nm . After adding CDs to the base solution, the absorption band broadens further with increasing pH, and the peak shifts slightly toward higher wavelengths. CDs alone display two distinct absorption bands at approximately 260 nm and 330 nm . The absorption intensity decreases with the pH of the solution in which the CDs are dissolved (Fig. 3(a)). The more alkaline the solution in which the CDs are suspended, the broader their absorption bands appear. This absorption behavior across the entire range corresponds to $\pi-\pi^*$ electronic transitions. CDs dissolved in various organic solvents exhibit different absorption behaviors depending on the solvent properties (Fig. 3(b)). Three distinct absorption regions can be identified in water, methanol, ethanol, glycerol, and polyethylene glycol (PEG). In these solvents, CDs show strong absorption below 300 nm . Additional absorption bands are observed with maxima at 330 nm and 410 nm . Among these solvents, glycerol results in the most intense absorption, with the 330 nm band being more prominent than the 410 nm band. CDs absorb with similar intensity in PEG, although the ratio between the 330 nm and 410 nm bands is lower compared to glycerol. The highest $330/410\text{ nm}$ band ratio is observed in water and ethanol, suggesting that CDs in these solvents exhibit minimal absorption in the visible region. In methanol, this ratio decreases, indicating that CDs can absorb visible light more effectively. In contrast, when CDs are dispersed in pentanol or acetonitrile, absorption is restricted to wavelengths below 250 nm and is of very low intensity. This suggests that these two solvents are not suitable media for dispersing CDs. This means that the greater the number of available OH groups in the solvent, the higher the intensity of the absorption band at 330 nm (Fig. 3(c)). Furthermore, a higher ratio of hydroxyl groups to carbon atoms in the solvent appears to promote the appearance of visible-range absorption features. The enhanced absorption at 330 nm and in the visible range in solvents with

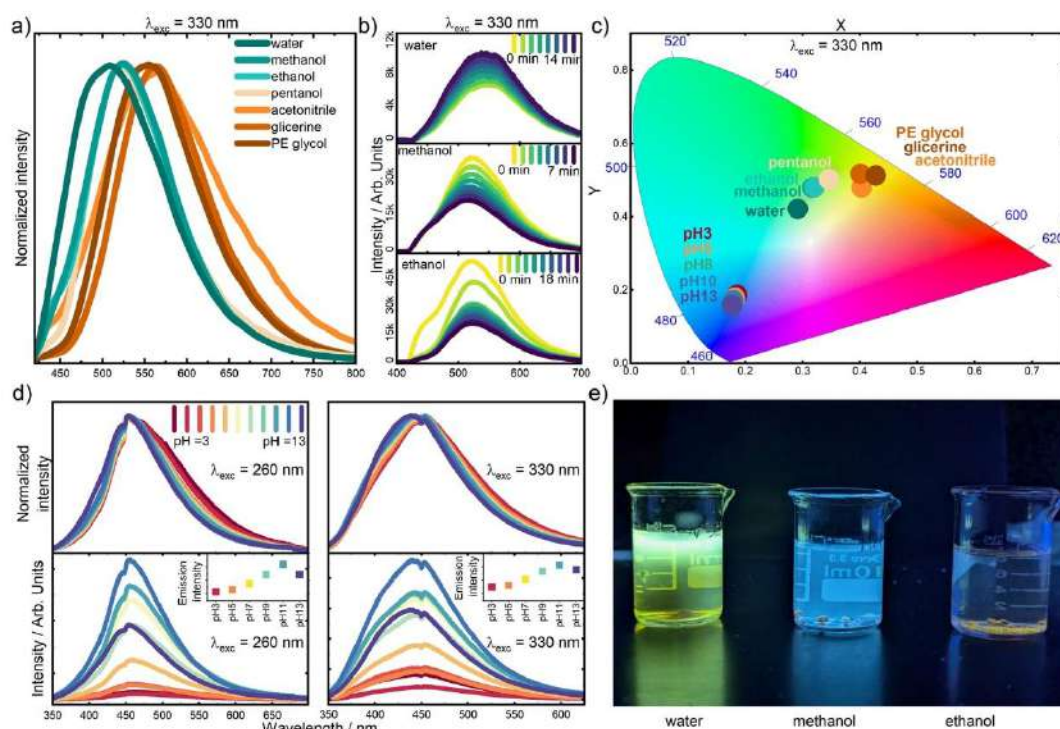


Fig. 4 (a) Emission spectra of carbon dots in different organic solvents, (b) time-based emission measurements in water, methanol and ethanol under 330 nm irradiation, (c) CIE diagrams for carbon dots in different solvents, (d) emission spectra in solutions with different pH under 260 and 330 nm irradiation, (e) Image of carbon dots in different solvents under UV light.

more hydroxyl groups (e.g., glycerol, PEG, water, ethanol) suggests a strong interaction between the solven's hydroxyl groups and the surface functionalities of the CDs. These interactions, likely hydrogen bonding, can stabilize certain electronic states within the carbon dot structure, leading to changes in their electronic transitions. Specifically, hydrogen bonding with surface hydroxyl or carboxyl groups on the CDs might alter the energy levels of the π and π^* orbitals of the graphene-like core and/or the surface states, making certain transitions (like the one at 330 nm, often associated with $n-\pi^*$ transitions of surface functional groups or charge transfer states) more probable or shifting their energy. Solvents with higher hydroxyl content might create a more extensive hydrogen-bonding network around the CDs, influencing their electronic structure and absorption properties more significantly.

PL spectroscopy was employed to investigate the emission behavior of CDs under various excitation conditions and to evaluate the influence of solvents and pH on emission intensity and wavelength shifts. The emission spectra in Fig. 4(a) were obtained under 330 nm excitation, showing the emission of CDs after complete dissolution in different solvents. Based on the results, a shift in the emission maximum is observed depending on the solvent. In water, the emission maximum is at 510 nm, whereas in alcohols, it shifts to approximately 525 nm. Interestingly, with increasing carbon chain length in alcohols, the emission maximum shifts slightly toward longer wavelengths. The use of solvents with a longer carbon chain, as

well as a larger number of hydroxyl groups, causes a greater shift towards longer wavelengths. However, the use of acetonitrile, a polar aprotic solvent with a lone electron pair, results in a shift of the emission maximum towards longer wavelengths and a broadening of the emission band. Similar trends are observed in the CIE diagram (Fig. 4(c)), where a redshift is evident with increasing carbon chain length and the presence of hydroxyl groups. Additionally, for CDs dispersed in water, methanol, and ethanol, time-dependent emission measurements were performed to investigate the evolution of their photoluminescence behavior (Fig. 4(b)). The emission spectra exhibit distinct temporal trends, depending on the solvent used. In water, the emission intensity gradually increases with time, while in alcohols—both methanol and ethanol—it decreases. Moreover, in methanol, a blue shift of the emission maximum is observed, accompanied by the emergence of a new emission band at ~ 450 nm. A similar additional band briefly appears in ethanol but disappears over time. This contrasting trend can be explained by solvent-dependent interactions with the CDs surface, including hydrogen bonding, polarity effects, and dynamic solvation. In water, the high polarity and extensive hydrogen-bonding network may initially quench surface states; however, over time, a reorganization of the hydration shell or disaggregation of aggregates may expose or activate emissive sites, leading to enhanced fluorescence. In contrast, in methanol and ethanol, the emission decreases with time, which may result from progressive solvent evaporation and

surface restructuring. In water, the high polarity and extensive hydrogen-bonding network may initially quench surface states; however, over time, a reorganization of the hydration shell or disaggregation of aggregates may expose or activate emissive sites, leading to enhanced fluorescence. In contrast, in methanol and ethanol, the decrease in emission intensity over time, linked to 'progressive solvent evaporation and surface restructuring,' suggests a different mechanism. As methanol/ethanol evaporates, the local concentration of CDs increases, potentially leading to increased aggregation-induced quenching. Additionally, the specific surface restructuring induced by alcohol evaporation might favor non-radiative decay pathways. The IR data (faster changes in methanol) support the idea that these alcohols, especially methanol, more effectively penetrate the CD aggregates, potentially altering the surface chemistry in a way that reduces quantum yield as the solvent leaves. This could involve the irreversible formation of new non-emissive states or the collapse of emissive structures. IR spectroscopy confirms that both alcohols induce notable, time-dependent changes in the CDs surface environment, particularly in methanol, where rapid changes suggest stronger penetration into CDs aggregates. The observed blue shift and the appearance of the 450 nm band in methanol likely indicate the formation of intermediate surface molecules or changes in the emission domains resulting from the interaction of solvent molecules with functional groups. The subsequent disappearance of this feature in ethanol over time suggests a reversible interaction or stabilization toward a dominant emission configuration. These findings highlight how solvent properties, specifically, hydrogen bonding capacity, molecular size, and volatility, determine time-dependent photoluminescence through their impact on surface state accessibility and solvation dynamics. Fig. 4(e) presents an image showing the emission of CDs in water, methanol, and ethanol immediately after mixing them with solvents.

To quantitatively evaluate the photoluminescence performance under different solvent conditions, quantum yield (QY) measurements were performed. QY values were determined for CDs dispersed in water, methanol, ethanol, and pH 13 solution. The corresponding QY values were 15% (water), 11% (methanol), 22% (ethanol), and 13.5% (pH 13 solution), with all measurements initially prepared using 2 mg CD per 5 mL solvent. However, due to differences in the solubility of CDs in the solvents, the actual dispersion homogeneity and optical density of the solutions were different. Especially in alcohols, differences in polarity, hydrogen bonding capacity, and solvent viscosity led to distinct solvation environments. As a result, direct comparison of QY values between solvents is not straightforward, as aggregation, sedimentation, and reabsorption effects can affect the emission performance. Additional QY measurements for CDs in methanol at different concentrations revealed a maximum QY of 18% for lower concentrations, confirming that the emission efficiency is highly dependent on the aggregation state and concentration-dependent quenching effects (Table S1 and Fig. S6, ESI†). These values are consistent with previously reported quantum yields for carbon dots synthesized *via* green methods without surface doping,

typically range from 10% to 20%.^{33–35} In comparison, CDs doped with nitrogen or sulfur can achieve much higher QY values, often exceeding 40%.^{33,36,37} The observed solvent-dependent differences in QY can be attributed to several factors. Stronger hydrogen bonding and solvation effects in methanol (confirmed by IR analysis) favor surface restructuring and emission quenching. The lower polarity and larger molecular size of ethanol limit the penetration of CD aggregates, leading to better preservation of the emissive surface states. At high pH, surface deprotonation changes the electronic structure of the surface groups, increasing emission but potentially introducing non-radiative decay paths. These results confirm that quantum yield is a strongly environment-dependent parameter for carbon dots and should be interpreted in the context of solvent properties, concentration, and colloidal stability.

CDs emission measurements in solutions with different pH are shown in Fig. 4(c) and (d). They were performed using two excitation wavelengths: 260 and 330 nm. In both cases, it can be observed that as the pH increases, the emission spectrum shifts towards shorter wavelengths. This trend is opposite to that observed in organic solvents. It highlights the role of hydroxyl groups, whether covalently bound within solvent molecules, such as in alcohol, or present as free hydroxide ions in basic aqueous solutions, in influencing the photoluminescence of CDs. The pH-dependent emission shifts are likely due to changes in the protonation/deprotonation state of surface functional groups on the carbon dots, such as carboxyl (–COOH) and hydroxyl (–OH) groups. As the pH increases (*i.e.*, a more basic solution), these acidic groups become deprotonated (*e.g.*, –COOH becomes –COO[–], and –OH becomes –O[–]). Deprotonation alters the electronic environment of the chromophores on the CD surface, resulting in changes to their energy levels. A blue shift (shorter wavelength emission) with increasing pH suggests that deprotonation might stabilize the excited state less or increase the band gap of the emissive states. This is often observed when deprotonation reduces electron-donating character or increases the energy required for electron transitions. The opposite trend compared to alcohols suggests that the mechanism of interaction of free hydroxide ions (in basic solutions) with the CD surface is fundamentally different from the interaction of covalently bound hydroxyl groups within alcohol molecules, which might induce different solvation effects or electronic rearrangements leading to distinct emission behaviors. A significant relationship that can also be observed in these spectra is that the emission intensity increases with increasing basicity of the solution. A similar relationship could also be observed in time-dependent measurements of CDs emission in water, methanol, and ethanol. It is visible that adding alcohol causes a significant increase in the emission intensity compared to the measurement of CDs in water, where the intensity decreases.

Conclusions

Based on the studies, several important conclusions regarding the properties and potential applications of the synthesized

CDs can be drawn. Using a simple combustion method, we enabled the synthesis of a material with a broad pH sensitivity range (1–14), characterized by continuous emission blue shift and a unique ability to distinguish organic solvents based on emission changes. CDs exhibit clear differences in emission depending on the type of alcohol, which allows for the distinction of methanol and ethanol, a feature relevant, for example, in detecting toxic methanol in beverages. IR spectroscopy revealed dynamic changes in the surface structure of CDs during solvent evaporation; methanol induces faster changes than ethanol, indicating differences in interactions with CDs aggregates. The observed shifts in emission wavelength depending on carbon chain length and the presence of hydroxyl groups confirm the strong influence of intermolecular interactions on the photoluminescent properties of CDs. In the pH range, an opposite trend in emission shift is observed (blue shift with increasing pH) compared to organic solvents (red shift). This highlights the importance of how hydroxyl groups are introduced, whether as components of solvent molecules or as ionic species, in modulating the photoluminescence of CDs. The emission can change over time, suggesting equilibrium processes at the surface and dynamic interactions with the medium, such as solvent evaporation or reorganization of the surface structure. The results indicate that the synthesized CDs are highly promising materials for low-cost, selective, broad-range environmental sensors and biomedical diagnostics.

Author contributions

Daniela Kujawa: conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing original draft. Maciej Ptak: formal analysis, investigation, writing original draft. Paweł Gluchowski: supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article are available at Zenodo.org at <https://doi.org/10.5281/zenodo.15526128>.

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Supporting Information

A Rapid, Green and Cost-Effective Synthesis of pH- and Hydroxyl Group Sensitive Carbon Dots for Sensing Applications

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Results

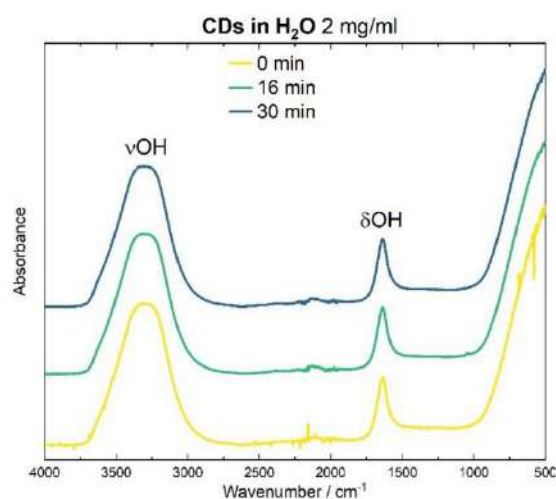


Figure S1. The time evolution of IR spectra collected for a 2 mg/ml suspension of CDs in water;

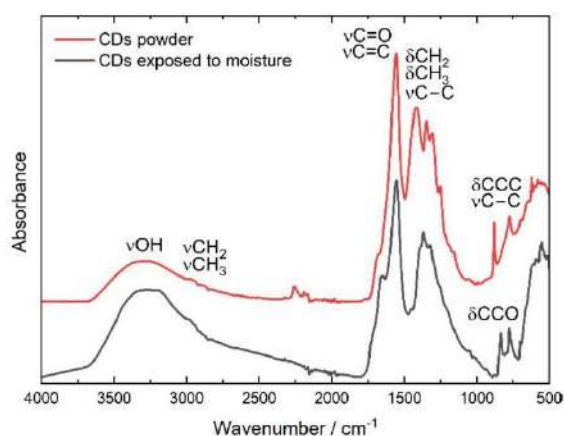


Figure S2. The reference ATR spectra of pristine CDs powder and powder exposed to moisture in air (after two weeks).

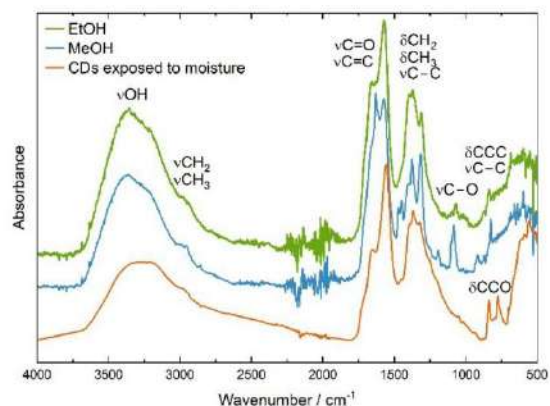


Figure S3. A comparison of ATR spectra of CDs exposed to moisture and after the experiments when suspended in MeOH and EtOH.

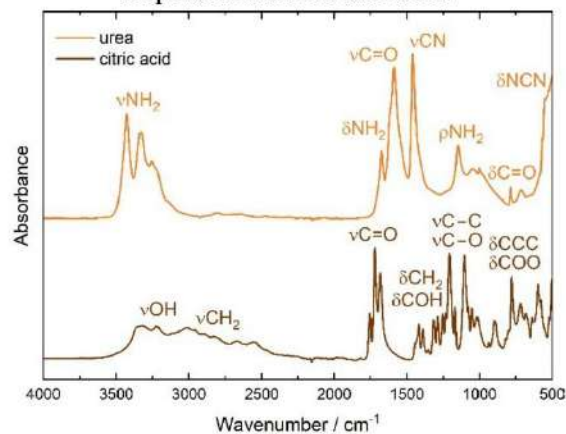


Figure S4. The reference ATR spectra of polycrystalline citric acid and urea.

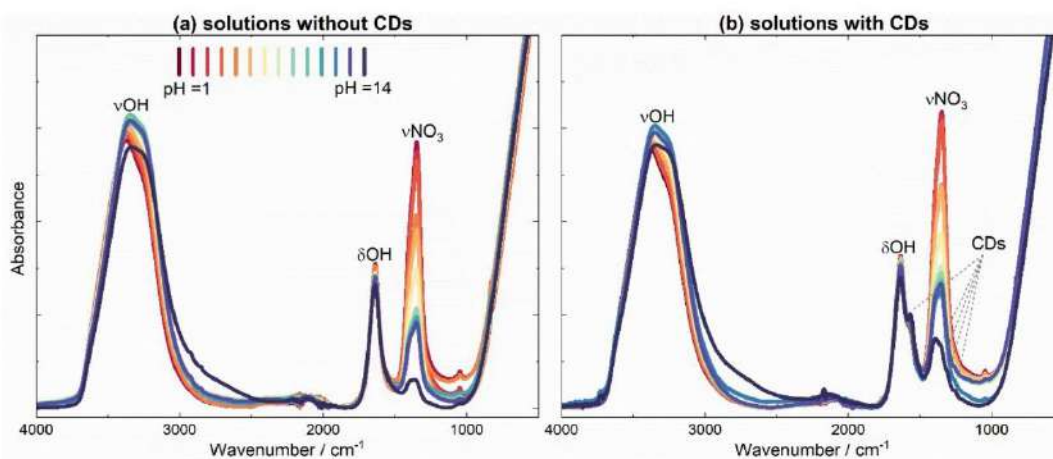


Figure S5. The ATR spectra measured for pH-dependent solutions without (a) and with (b) CDs (2mg/ml).

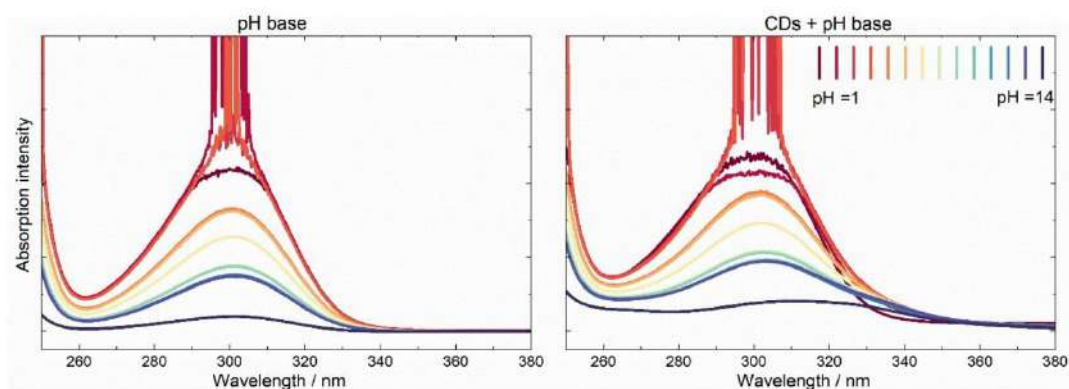


Figure S6. The absorption spectra of pH base and base with CDs.

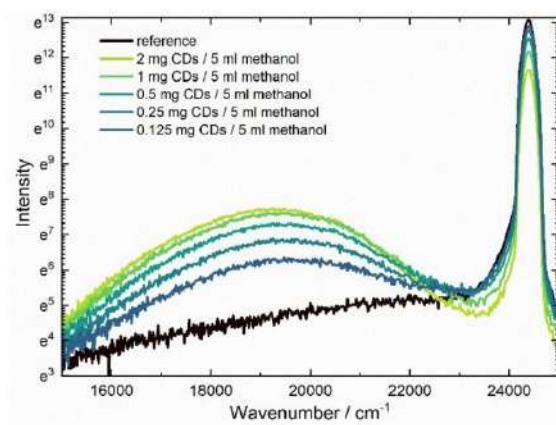


Figure S7. The fluorescence quantum yield of CDs in methanol at different concentrations.

Table S1. Comparison of fluorescence quantum yield for CDs in methanol at different concentrations.

Concentration of CDs in methanol	QY
1mg / 5ml	16.36%
0.5mg / 5ml	17.49%
0.25mg / 5 ml	18.00%
0.125mg / 5 ml	16.44%

8.1.3. Increasing photocatalytic activity and extending the absorption range of known photocatalysts by creating hybrid structures with carbon dots (published)

The P3 publication focuses on effectively combining the optical properties of CDs with TiO_2 to develop a highly efficient hybrid photocatalytic system. The primary research goal was to enhance the photocatalytic activity of TiO_2 , a widely used semiconductor, by developing a hybrid material incorporating CDs. The key factor determining the efficiency of the developed systems is the structural difference between the two semiconductor matrices, $\text{TiO}_2(1)$ and $\text{TiO}_2(2)$. The $\text{TiO}_2(1)$ matrix possesses a highly developed porous structure with a large specific surface area and wide pores, which allows for the effective accommodation and uniform dispersion of carbon dots within its channels. In contrast, $\text{TiO}_2(2)$ has smaller surface area and narrow pores that restrict the entry of CDs, causing them to aggregate on the outer surface and block active catalytic sites. Modification with fluorescent dots (CDs) only shifts the absorption edge toward visible light without increasing catalytic activity. However, using phosphorescent materials (PhCDs) slows charge-carrier recombination by trapping electrons in levels below the conduction band, enabling the hybrid material to undergo photocatalytic processes under solar radiation. This hybrid material design strategy enables the effective utilization of free, renewable solar energy, a key aspect of sustainable environmental cleaning technologies.

As part of the work, a hybrid material was developed, consisting of a porous TiO_2 matrix with a high specific surface area and carbon dots. The hybrid material was prepared by impregnation with fluorescent or phosphorescent carbon dots, ensuring intimate contact between the CDs and the semiconductor, which is essential for efficient charge and energy transfer. Analysis of changes in the specific surface area and pore distribution confirmed the presence of CDs within the pores. The key and most innovative aspect of this work is the use of PhCDs to enhance photocatalytic processes. While pure TiO_2 exhibits activity primarily in the UV range and its efficiency is limited by rapid electron-hole recombination, the P3 publication demonstrated several advantages of the hybrid system:

- Increased absorption range - Absorption studies confirmed the possibility of using visible light to activate the system

- Role of triplet states - PhCDs promote more efficient generation of ROS. The use of long-lived triplet states extends the time window during which energy transfer to oxygen and water molecules adsorbed on the catalyst surface is possible, which increases the efficiency of radical generation compared to short-lived singlet states.
- Charge separation - the carbon material acts as an electron trap, effectively inhibiting electron-hole recombination and extending their availability for pollutant degradation reactions (Fig. 10).

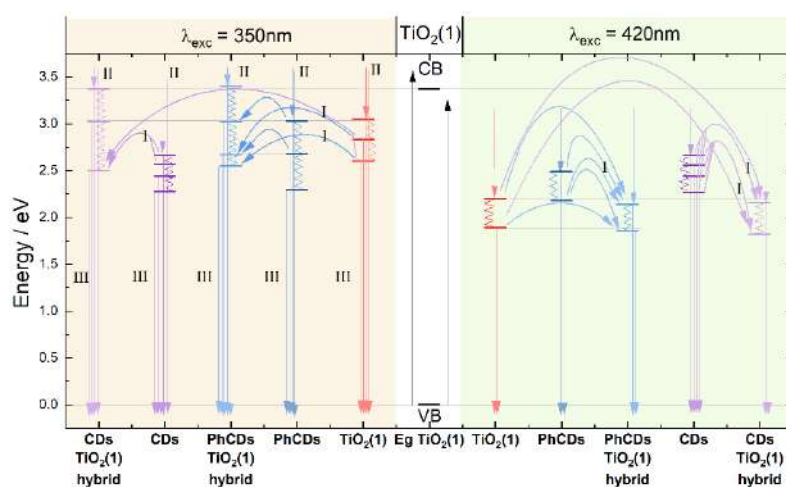


Figure 10. Mechanism of energy transfer in $\text{TiO}_2(1)$, PhCDs, CDs, and hybrid materials.

Reprinted with permission from [156].

The effectiveness of the strategy for enhancing photocatalytic activity was demonstrated in the CBZ removal process. The results confirmed that the hybrid system is more efficient than pure TiO_2 , achieving almost complete degradation of the pharmaceutical. Additionally, the work includes a detailed analysis of the degradation mechanism and identification of intermediate products, confirming that the process leads to effective mineralization of the contaminant (Fig. 11) (Table 4.).

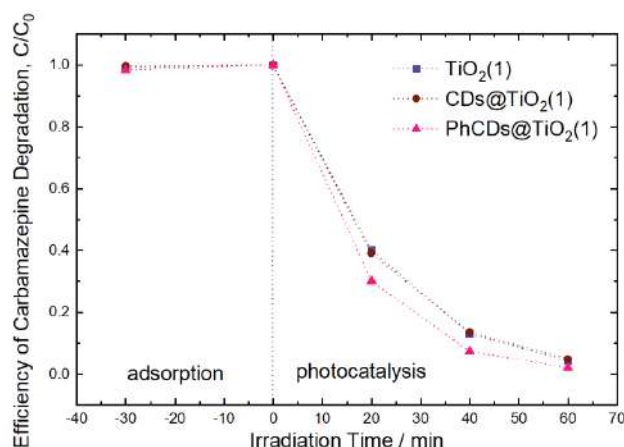


Figure 11. Efficiency of carbamazepine degradation for (a) pure $\text{TiO}_2(1)$ and hybrid materials $\text{PhCDs@TiO}_2(1)$ and $\text{CDs@TiO}_2(1)$. Reprinted with permission from [156].

Table 4. Photocatalytic activity of the prepared samples

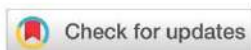
Sample name	Carbamazepine degradation efficiency (%)	Degradation rate constant $k \cdot 10^{-2} \text{ (min}^{-1}\text{)}$	Efficiency of TOC reduction (%)
$\text{TiO}_2(1)$	95.8	5.31	50.7
$\text{CDs@TiO}_2(1)$	95.3	5.11	2.4
$\text{PhCDs@TiO}_2(1)$	98.0	6.59	60.2
$\text{TiO}_2(2)$	61.8	1.60	0
$\text{CDs@TiO}_2(2)$	42.6	0.93	0
$\text{PhCDs@TiO}_2(2)$	60.8	1.56	0

In conclusion, this work demonstrates that CDs can be a breakthrough functional component for modifying existing photocatalysts. The most important aspect of this work is the demonstration that integrating CDs with TiO_2 overcomes the energy barriers of classical photocatalysis, enabling efficient operation of the system in the visible-light range.

Author contribution to the publication P3

conceptualization, synthesizing CDs, preparing hybrid materials, preparing materials for structural and morphological studies, performing spectroscopic measurements, processing data and preparing their graphic visualization, analyzing the results, planning the structure of the manuscript, proposing the energy transfer mechanism, preparing the

initial and final versions of the manuscript, preparing responses to reviewers, archiving data after preparing the final article



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Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst†

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This study focuses on harnessing the synergistic effects between titanium oxide (TiO₂) and carbon dots (CDs) to enhance the photocatalytic performance of TiO₂. The work describes the synthesis of carbon dots exhibiting fluorescence (CDs) or phosphorescence (PhCDs), as well as the preparation of the TiO₂ hybrid. Structural and textural measurements (X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂ sorption isotherms) were conducted to elucidate the compositional and morphological changes induced by the incorporation of CDs into a matrix. Spectroscopic analyses revealed a shift of the absorption edge and range into the visible region of the CDs@TiO₂ hybrid compared with pure TiO₂. Infrared (IR) and Raman spectroscopy revealed the presence of diverse bonds associated with functional groups on the surface of the dots, enabling control over the spectroscopic properties of the resulting hybrids. Photocatalytic assessments demonstrated an enhancement in the PhCDs@TiO₂ hybrid activity compared with pure TiO₂. The proposed mechanism for the increase in photocatalytic activity in PhCDs@TiO₂ is based on the slowdown of carrier recombination, which is linked to the confinement of electrons within traps located below the conduction band. The demonstrated enhancement in photocatalytic activity holds promise for the more effective decomposition of organic compounds in water, while the utilization of carbon dots unveils new avenues for modifying existing photocatalysts.

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1. Introduction

Photocatalysis phenomena on TiO₂ and zinc oxide semiconductors have been studied since the 1960s. During these studies, it was found that some compounds, such as O₂ or H₂O, were adsorbed or desorbed on the surface of the solid under the influence of UV light, depending on the surface conditions. This phenomenon was explained by the band theory of semiconductors which explains how electrons behave in such materials. It highlights two key energy bands: the valence band (VB), where electrons are tightly bound to atoms, and the conduction band (CB), where electrons can move freely. The energy gap between these bands, called the band gap, deter-

mines the conductivity properties of a semiconductor. When electrons absorb energy, they are transported from the VB to the CB, and when they return to the VB, the excess energy is released.^{1–4} The first important research on the photocatalysis process on a TiO₂ photocatalyst using UV light was described by Masuo in 1964.⁵ Honda and Fujishima⁶ discovered the photosensitization effect on TiO₂ electrodes in 1972 and used it to split water, which was performed at a much lower bias voltage compared with normal electrolysis. These processes were performed using Pt electrodes as the cathode and TiO₂ as the photoanode. Further research was focused on improving photolysis using TiO₂.^{7,8} This material is a very good photocatalyst, which works with high efficiency, but the main disadvantage is that it absorbs only UV light and cannot work in the visible range. That is why researchers focus on finding new materials or using TiO₂ coupled with other materials that have similar or better efficiency and can also absorb visible light.

Materials that in recent years focused the research on adapting photocatalysis to the visible range are CDs, which can play different roles in this process. CDs themselves can be used as photocatalysts because of their strong ability to absorb

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4dt02196g>

light, excite electrons and generate holes. These materials can also act as electron donors and/or acceptors. The nature of the dots is defined by the amount and type of functional groups on the surface.⁹ They have the ability to absorb energy and emit photons with energy higher than that absorbed. It means that they can be used as up-converters.¹⁰ This property is useful during photocatalysis for many hybrid systems consisting of dots attached to the surface of semiconductors with a wide bandgap. The CDs can absorb long-wavelength visible or infrared light and emit a photon in the ultraviolet range, which then excites electrons in a wide-band semiconductor. This allows such materials to work indirectly in visible light.¹¹

For photocatalytic applications, the CDs are embedded in porous materials. This prevents the aggregation of nanoparticles and improves their optical performance.¹² In this case, many researchers are using metal-organic frameworks (MOFs), which are one-, two- or three-dimensional structures. MOFs are formed by metal ions or metal clusters and organic ligands.^{13,14} This material is a good example of a scaffold for CDs that can be used in photocatalytic applications. MOF with encapsulated dots exhibits high photostability, tunable photoluminescence, rapid electron transfer, and up-conversion luminescence.^{15–18} Raw MOF is not often used as a photocatalyst because it does not have sufficient ability to absorb light and recombine the charges which are generated by light. CDs can absorb light with higher efficiency. Moreover, their structure provides faster transmission of photogenerated electrons and transforms dots into electron acceptors. Hybrids of MOFs and CDs are used as photocatalysts because they form a structure with many active sites, similar to semiconductors. Each active site in MOFs, such as a metal-oxygen cluster, can be considered a single quantum dot, acting as a light absorber, charge generator, and catalytic site, much like a small semiconductor. Additionally, organic linkers in MOFs can act as antennas, absorbing additional ultraviolet (UV) light and transferring energy to active sites *via* ligand-metal charge transfer (LMCT).¹⁴ Adding carbon dots to that structure could shift the absorption edge to the visible light and slow electron-hole recombination, improving the photocatalytic process.^{19–22}

CDs have also been introduced into commonly known and used photocatalysts to improve their photocatalysis process. The TiO₂ semiconductor is used in photocatalysis due to its possible double-walled structure, characterized by a large specific surface area and porosity.²² It has been shown that titanium oxide in the anatase structure exhibits better photocatalytic activity compared with rutile or brookite. Augustynski²³ investigated all TiO₂ structures and found that the higher photocatalytic performance depends on the presence of surface-bound peroxy species, the formation of which is promoted by the lattice plane of anatase TiO₂. To extend the absorption range of anatase, carbon dots can be used as they absorb light mainly in the visible range.²⁴ Yin *et al.*²⁵ created an N,S-CQDs-TiO₂ hybrid (CQDs – carbon quantum dots, which are a subgroup of CDs always showing a spherical structure and crystalline structure with functional groups on the

surface) that was able to generate H₂ when exposed to light. After preparing such a hybrid, they obtained 77% better results in generating H₂ during light exposure than for pure CDs. The conduction band of TiO₂ acts as an electron intermediate that efficiently transfers electrons from the inert to the active band of CDs (responsible for H₂ generation). Zhang *et al.*²² obtained CQD/TiO₂ nanotubes (NT), which utilized up-conversion emission from carbon dots to degrade rhodamine B in the visible light range. Zhang *et al.*²⁴ prepared hybrids of CQD with TiO₂ NT, which can absorb visible light and near-infrared radiation, promoting charge separation and electron transfer. That hybrid exhibits better photocatalytic properties in reducing CO₂ than pure TiO₂ NT. Mozdbar *et al.*²⁶ developed a hybrid material by combining carbon quantum dots with TiO₂ and investigated its photocatalytic activity under both visible and UV light. They found that the formation of this hybrid resulted in a shift of the absorption edge towards visible light and led to higher photocatalytic activity in methyl blue removal under visible light irradiation compared with pure TiO₂. It was demonstrated that carbon dots can be prepared to exhibit phosphorescence by embedding them in various matrices. The phosphorescence mechanism relies on the transfer of an electron from the singlet to the triplet state *via* intersystem crossing (ISC), a process in which spin multiplicity changes from a singlet state (paired electron spins) to a triplet state (unpaired electron spins). Once in the triplet state, the electron experiences a slower rate of decay, allowing for long-lasting phosphorescence to occur due to the forbidden nature of triplet-singlet transitions. The matrix in which the carbon dots are embedded plays a critical role in stabilizing the triplet state, often by limiting molecular vibrations or interactions that would otherwise quench the triplet state, thus extending the lifetime of the excited state. Phosphorescent carbon dots, where electrons are maintained in the excited triplet state for extended periods, can effectively reduce the recombination of electron-hole pairs, a significant limiting factor in photocatalytic processes. By slowing down recombination, phosphorescent dots improve the overall efficiency of photocatalytic reactions. In contrast, non-phosphorescent carbon dots, which do not benefit from this stabilization of excited states, exhibit faster recombination rates, which limits their potential in such applications.^{27–29}

The aim of this work was to increase the photocatalytic activity of anatase TiO₂ in the degradation of carbamazepine by incorporation of CDs into its pores. This was achieved by impregnating two types of TiO₂ with two types of CD. TiO₂ was obtained in two different ways: the well-known solvothermal reaction of TBT and acetic acid, and the unconventional route of thermal decomposition of Ti-based MOF. Both materials are in the anatase phase but have different sizes, shapes, porosities, and therefore different properties, so both were used to synthesize new hybrids. Two types of carbon dot were used to show the impact of their different spectroscopic properties on the photocatalytic activity. Luminescent CDs were added to shift the absorption edge of the TiO₂ to enable the use of the hybrid in a wider range of light (including the visible range).

Phosphorescent CDs also shift the absorption range, but additionally due to their longer emission decay (slower carrier recombination) allow an increase in the photocatalytic activity of the hybrid. It was assumed that the presence of CDs in the TiO_2 pores would increase the absorption of light in the visible range, and improve energy transfer in the semiconductor, and that by using dots exhibiting phosphorescence, the carrier recombination process will be slowed down. All the above changes will result in an increase in photocatalytic activity. A number of studies have been conducted to verify our thesis. For pure and hybrid materials, their structure, morphology, spectroscopic properties, textural properties, and photocatalytic activity were examined.

2. Experimental

2.1. Materials

Synthesis of carbon dots (CDs). Luminescent carbon dots (CDs) were prepared based on the article by Liu *et al.*³⁰ For the synthesis of CDs, 26 mg of 3,4,9,10-perylene tetracarboxylic dianhydride (PTDA, Alfa Aesar) was dissolved in 4 mL of distilled water and 1 mL of triethylamine (TEA, Alfa Aesar). The solution was placed in a Teflon vessel closed tightly in the stainless autoclave (reactor). The reactor was left in the oven for 48 hours at 220 °C. After the process, the solution was purified using a paper filter to separate larger particles. This solution was further filtered using a membrane filter (SIMAX) with a pore size of 0.22 μm . Phosphorescent carbon dots (PhCDs) were prepared according to the article by Ding *et al.*³¹ For the synthesis of PhCDs, 400 mg of citric acid (anhydrous, POCH, Poland) and 6 g of boric acid (99+%, Chempur, Poland) were dissolved in distilled water and then calcinated at 180 °C for 5 hours with a temperature rise step of 10 °C min^{-1} . The obtained powder was the final product of carbon dots.

Synthesis of TiO_2 . The anatase (TiO_2) was prepared using two synthesis methods to obtain mesoporous nanostructures. $\text{TiO}_2(1)$ was prepared by the known solvothermal reaction.³² Typically, 0.8 mL of titanium(IV) butoxide (TBT, 97%, Sigma Aldrich) was added dropwise while vigorously stirring into 40 mL of acetic acid (99.5–99.9%, Avantor Performance Materials Poland S.A.). After 30 min of mixing, the obtained white suspension was transferred to an autoclave (the same as in the CD synthesis) and maintained at 200 °C for 24 hours. After cooling to room temperature, the product was collected by centrifugation, washed with ethanol (96%, STANLAB Poland) (3×25 mL), and dried at 60 °C for 24 hours. Finally, to remove the residual organics, the precipitate was calcined at 400 °C for 30 min with a temperature rise step of 5 °C min^{-1} . $\text{TiO}_2(2)$ was prepared by the calcination of Ti-based MOF. Firstly, MIL-125(Ti)- NH_2 was accomplished using a solvothermal route as previously reported.³³ Typically, 2.71 g of 2-aminoterephthalic acid (90%, Sigma Aldrich) was stirred until dissolved in 50 mL of *N,N*-dimethylformamide (DMF, Avantor Performance Materials Poland S.A.), and then 2.96 mL titanium(IV) isopropoxide (TTIP, 97%, Sigma Aldrich) was

added followed by 12 mL of methanol. After 30 min of mixing the suspension was transferred to an autoclave and maintained at 150 °C for 24 hours. After cooling to room temperature, the product was collected by centrifugation, washed with DMF (3×25 mL) and methanol (99.8%, Avantor Performance Materials Poland S.A.), and dried at 60 °C for 24 hours. Then, the prepared MIL-125(Ti)- NH_2 was crushed by grinding in a mortar and calcined at 380 °C for 5 hours with a temperature rise step of 5 °C min^{-1} .

Preparation of CDs@TiO_2 . $\text{CDs@TiO}_2(1/2)$ and $\text{PhCDs@TiO}_2(1/2)$ hybrids were prepared by an impregnation method. For this purpose, 0.3 g of $\text{TiO}_2(1/2)$ was suspended in 20 mL of CD solution (0.56 mg in acetone) or PhCDs (300 mg in ethanol) using an ultrasonic bath. After 3 h of shaking on the platform (400 rpm) the powder was centrifuged and washed with 25 mL of the solvent in which the impregnation was carried out. Such prepared hybrids were then dried at 60 °C for 24 h.

2.2. Equipment

The XRD data were collected between 10 and 80 2 θ degrees. The measurements were carried out at room temperature using an X'PERT PRO PANalytical (Malvern Panalytical, Malvern, UK) diffractometer with $\text{CuK}\alpha_1$ radiation (1.5406 Å) and step 0.03°. The samples were examined using a Philips CM20 Super Twin operating at 160 kV and also a Tecnai G2 20 X-TWIN transmission electron microscope (TEM) equipped with a LaB_6 cathode electron gun, an FEI Eagle 2K CCD camera, and a high-angle annular dark-field (HAADF) detector for scanning transmission electron microscopy (STEM). Measurements were conducted at an accelerating voltage of 200 kV in both bright field and scanning and transmission modes. Additionally, measurements were taken with a Hitachi S-3400N scanning electron microscope (SEM), which featured a tungsten cathode gun, a secondary electron (SE) detector, and a backscattered electron detector. The pure TiO_2 samples were sputter-coated with gold using a Cressington 108A gold sputter coater. Imaging was carried out at an accelerating voltage of 10 kV. The N_2 adsorption-desorption isotherms were obtained at 77 K using a Micromeritics 3Flex Surface Characterization Analyzer. Prior to isotherm acquisition, the materials were activated and outgassed (150 °C, 1.3 kPa) for 12 h. MicroActive software was used to determine the specific surface area according to the Brunauer-Emmett-Teller (BET) method and total pore volume at a relative pressure (p/p_0) = 0.9.

The mid-IR spectra of all samples suspended in KBr pellets were measured using a Nicolet iSTM50 FT-IR spectrometer. The Raman spectra were measured using the micro-Raman apparatus (inVia™ Renishaw) with a 514 nm excitation line in the range 100–3200 cm^{-1} . Absorption spectra were measured with a Varian Model 5E UV-VIS-NIR spectrophotometer at room temperature in the range 200–800 nm in reflectance mode. The spectral bandwidth of the instrument was set to 0.1 nm. Based on the absorption spectra, the band gap of materials was calculated by using the Kubelka-Munk theory^{34,35} which is based on the measurement of diffuse

reflection and describes the behaviour of light inside a sample that scatters light. This theory is applicable to particles that are comparable in size to or smaller than the wavelength of the incident light. When the thickness of the samples does not exceed a certain limit, it does not influence the reflectance. It can then be described by the Kubelka–Munk function:

$$\frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = F(R_{\infty}) \quad (1)$$

Here, K and S are the absorption and scattering coefficients respectively, R_{∞} represents the diffuse reflectance, and $F(R_{\infty})$ is referred to as the Kubelka–Munk function. In materials with a parabolic band structure, the absorption coefficient and energy gap (E_g) are related through the well-known Tauc³⁶ relation. For different band gap materials, the Tauc relation is given by:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where α is the linear absorption coefficient, ν is the light frequency, A is the proportionality constant, and ' n ' is typically set to 1/2 for direct band gap materials. If the radiation scatters perfectly, the absorption coefficient K becomes equal to 2α , and the scattering coefficient remains constant concerning wavelength. The Kubelka–Munk function is proportional to α , and the relationship can be described as:

$$[F(R_{\infty})h\nu]^2 = A(h\nu - E_g) \quad (3)$$

In the next step, a graph of $(\alpha h\nu)^2$ vs. $h\nu$ was plotted, which facilitated the determination of the energy gap.

The emission spectra of TiO₂, carbon dots, and hybrid materials were measured using the FLS980 Fluorescence Spectrometer from Edinburgh Instruments (Livingston, UK), equipped with 1800 lines per mm holographic grating and 300 mm focal length monochromators in a Czerny–Turner configuration. To obtain the spectra, a 450 W xenon lamp was employed, and a Hamamatsu R928P side window photomultiplier tube (Hamamatsu Photonics, Shizuoka, Japan) served as the detector. The decay time was measured by using a femtosecond Libra laser (Coherent, USA) and Streak Camera (Hamamatsu, Japan) as a detector.

2.3. Photocatalytic analysis

The photocatalytic activities of the prepared materials were examined in the reaction of carbamazepine (CBZ) degradation. A CBZ solution concentration of 14 mg dm⁻³ (initial TOC value of 10.67 mg dm⁻³) was used, while the photocatalyst content was 2 g dm⁻³. The photocatalytic processes were performed in a glass reactor with a quartz window equipped in air supply mode and placed on a magnetic stirrer. In a typical experiment, 50 mg of the photocatalyst was dispersed in 25 cm³ of the CBZ solution. The irradiation source was a 300 W xenon lamp (LOT Quantum Design) with a light intensity in the UV range (310–380 nm) equal to 30 W m⁻². The spectrum of the lamp is presented in Fig. S1.† Before irradiation, the dark reaction was performed for 30 min to reach the adsorption–desorp-

tion equilibrium. Experiments were conducted at a constant temperature of 20 °C. Samples (2 cm³) were collected at 0, 20, 40, and 60 min during the photocatalysis process. The suspension was filtered using a 0.2 µm syringe filter to separate the photocatalyst from the solution. The progress of CBZ degradation was monitored using reverse-phase high-performance liquid chromatography (Shimadzu UFLC LC-20AD Kyoto, Japan) with a photodiode array detector (Shimadzu SPD-M20A). The parameters of the HPLC measurement are listed in Table S1.† The mineralization efficiency, measured as the total organic carbon (TOC) removal, was measured using a Shimadzu TOC analyzer.

Further experiments were conducted to investigate the influence of the photocatalyst dosage (0.5, 1 and 2 g dm⁻³) and carbamazepine (CBZ) solution concentration (8.5, 14 and 19.5 mg dm⁻³) on the efficacy of the photocatalytic process. Additionally, trapping experiments were performed using scavengers (10 mM) to elucidate the reactive species involved in pharmaceutical degradation. Ammonium oxalate was employed as a hole scavenger, *tert*-butanol as a hydroxyl radical scavenger, ascorbic acid for trapping superoxide anion radicals, and sodium azide as a singlet oxygen scavenger.

3. Results and discussion

3.1. Structure and morphology

X-ray diffraction (XRD). The XRD diffractogram (Fig. 1) shows the structure of the pure materials as well as the hybrids. The TiO₂ has an anatase phase (ICSD #9855), and no impurities of other phases were found. In the XRD pattern of PhCDs, peaks were found that are attributed to the boric acid *P*1 space group (ICSD #52290), which shows the presence of a polycrystalline boric acid matrix. The CDs show a broad band centred at around 23 2θ degrees that is characteristic of the graphene structure.³⁷ Hybrid materials with PhCDs and CDs show a structure assigned to the anatase phase of the TiO₂ framework. The hybrid materials change colour from white to grey after impregnation (Fig. S2†), indicating that the PhCDs/CDs are incorporated into the pores of the TiO₂. On the other hand, in the XRD of the hybrid materials, no peaks/bands from the graphene material can be seen, which leads to the conclusion that the content of carbon dots in the TiO₂ pores is less than 5%. For hybrid structures, an increase of FWHM (full width at half maximum) of the peaks can be observed compared with the diffractogram for TiO₂ (Table 1). The increasing FWHM peaks could result from increasing a structural disorder³⁸ or increasing the tensile stress in the material.³⁹ To test both theories, the strain was calculated from the XRD diffraction pattern. It was shown that after impregnation, the strain increased for almost all samples except PhCDs@TiO₂(1), where strain decreased.

SEM/TEM. SEM and TEM images revealed that nanometer-sized, spindle-shaped particles of TiO₂(1) are about 200 nm long and 120 nm wide (Fig. 2a and c). In the TEM image (Fig. 2a) it can be seen that the particle surface is highly

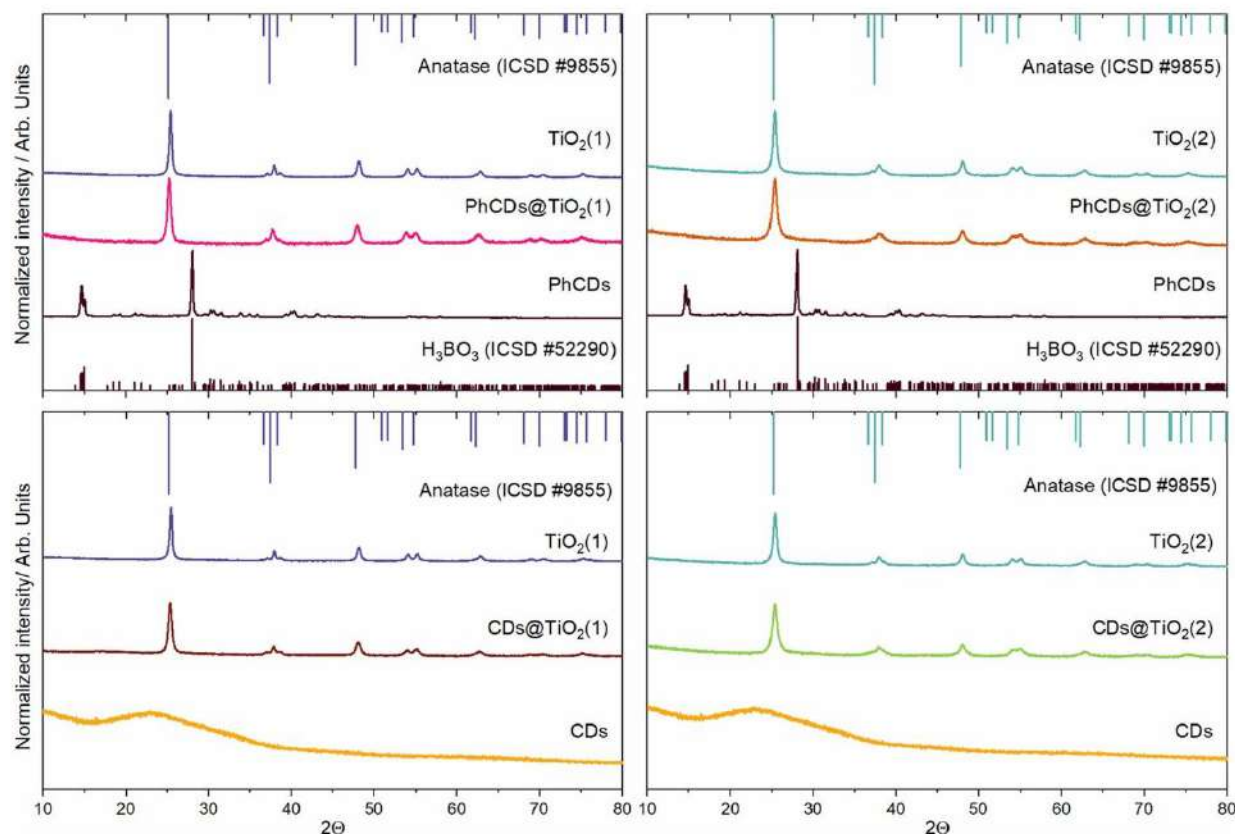


Fig. 1 XRD diffractogram for raw TiO_2 , carbon dots and hybrid materials.

Table 1 FWHM value of peak observed at 25.5° of pure TiO_2 and hybrid materials

Sample	Strains, %	FWHM, $^\circ$
$\text{TiO}_2(1)$	0.071	0.3711
$\text{PhCDs@TiO}_2(1)$	0.052	0.5188
$\text{CDs@TiO}_2(1)$	0.083	0.5274
$\text{TiO}_2(2)$	0.071	0.5292
$\text{PhCDs@TiO}_2(2)$	0.091	0.7201
$\text{CDs@TiO}_2(2)$	0.082	0.7426

porous with pores with a diameter of approximately several nanometers, whereas $\text{TiO}_2(2)$ retained the shape of the initial MOF resulting in square-shape particles with a side length close to 220 nm (Fig. 2b). Compared with $\text{TiO}_2(1)$, $\text{TiO}_2(2)$ has a compact structure with much lower porosity.

TEM images of hybrid materials show that the morphology and size of the grains do not change after impregnation (Fig. 3). It can be observed that after impregnation, the $\text{TiO}_2(1)$ (Fig. 3a and c) structure shows a lower porosity than before impregnation. In the TEM image of the $\text{TiO}_2(2)$ hybrid, small grains can be seen on the surface of the titanium dioxide (Fig. 3e and g). This indicates that carbon dots are located partially in the pores but also on the surface of the photocatalysts. The CDs can be observed as nanostructures with a diameter of

less than 10 nm (Fig. 3b and f). It can also be observed that the hybrids have planes with an interplanar spacing of 0.33–0.35 nm, which is a characteristic value for a graphene multilayer structure present in CDs as well as TiO_2 for the (101) plane of the anatase phase.^{40,41} Therefore, it is not possible to determine from the TEM images if the smallest particles on the surface are TiO_2 or CDs, but based on the spectroscopic results presented later, it can be concluded that they are CDs.

The Brunauer-Emmett-Teller (BET) method. To calculate the surface area of both types of titanium oxide as well as to check the impact of the impregnation of the structures with the CDs, the Brunauer-Emmett-Teller (BET) method was used. The textural properties of TiO_2 and CDs@TiO_2 were characterized by nitrogen sorption measurements. The obtained materials display type IV isotherms, which is a characteristic feature of mesoporous materials (Fig. 4). The BET surface area of TiO_2 varied notably depending on the method of synthesis and was determined to be $106 \text{ m}^2 \text{ g}^{-1}$ and $68 \text{ m}^2 \text{ g}^{-1}$ for $\text{TiO}_2(1)$ and $\text{TiO}_2(2)$, respectively, while the total pore volume was nearly identical for both materials (Table 2). Due to the occupation of the pores, the BET surface area decreased more for both types of TiO_2 after impregnation with CDs (Table 2).

Raman spectroscopy. The Raman spectra for CDs, TiO_2 , and hybrid materials are shown in Fig. 5. The spectra for TiO_2 and

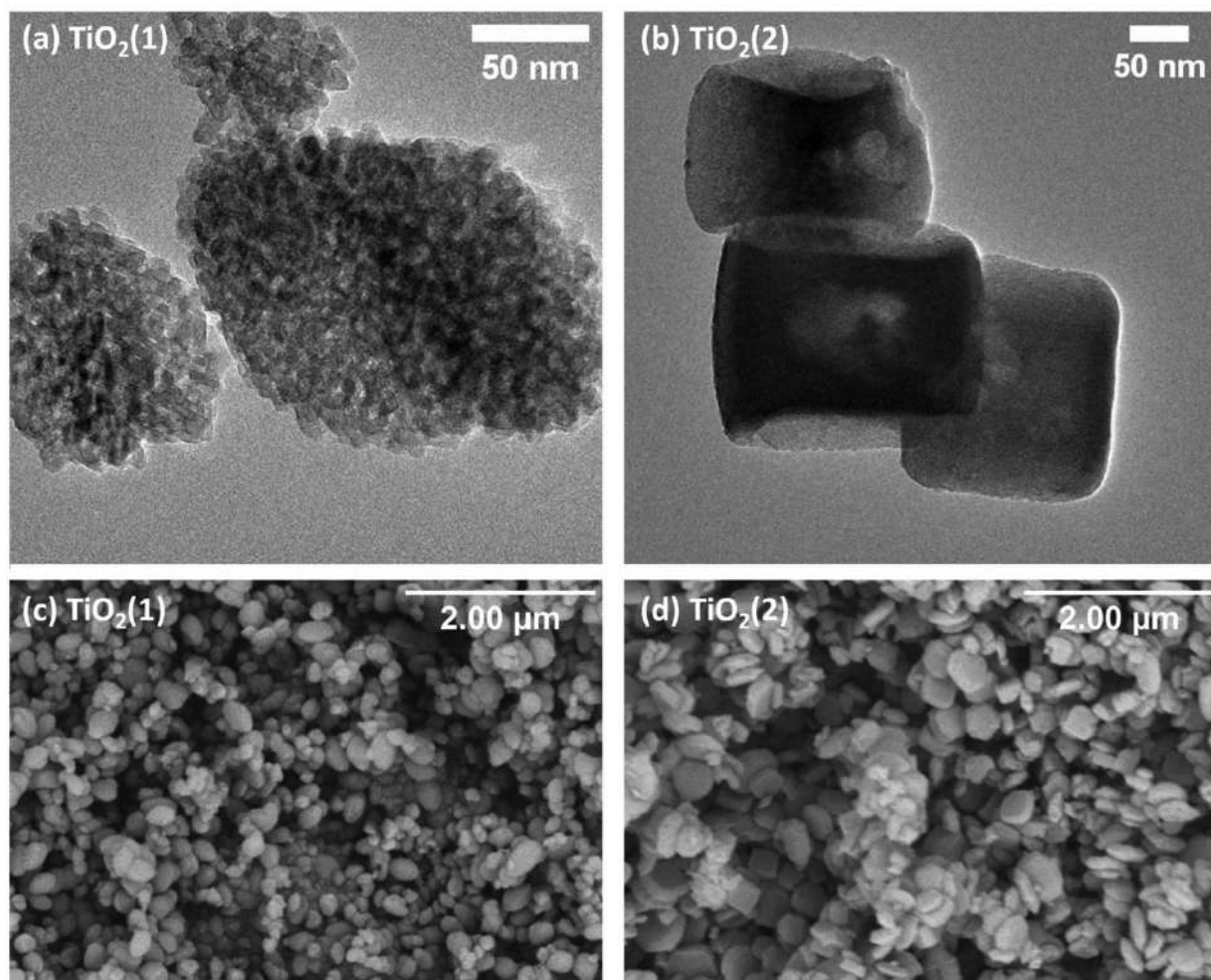


Fig. 2 TEM (a and b) and SEM (c and d) images of $\text{TiO}_2(1)$ (a and c) and $\text{TiO}_2(2)$ (b and d).

the hybrid materials show peaks at approximately 145, 396, 520, and 637 cm^{-1} , which correspond respectively to E_g , B_{1g} , B_{1g} , E_g modes of the anatase phase. Peaks located at 145 cm^{-1} are assigned to the Ti-Ti bonds in the unit cell. The E_g modes arise in Raman spectra when the symmetric stretching vibrations of O-Ti-O are present, and the symmetric bending vibrations of O-Ti-O are characterized by B_{1g} modes.^{42–44} In the results from the hybrid materials, the peaks from the oxide dominate because the content of carbon dots in the hybrid material is low. Additionally, carbon dots are structures much smaller than the size of TiO_2 , and the signal from carbon dots is faintly measurable. The PhCDs spectrum shows peaks at approximately 208 and 497 cm^{-1} , which are characteristic respectively of E_{2g} , and 882 cm^{-1} , for A_g modes of the boric acid structure. The first E_{2g} band at 208 cm^{-1} is characteristic of lattice translatory oscillation, and the second is associated with bending vibrations of O-B-O. The A_g mode observed in the spectrum arises when the stretching vibration of B-O is present.^{45,46} The CDs spectrum exhibits peaks that could be assigned to the D and G bands of graphene.⁴⁷

IR spectroscopy. Infrared spectroscopy measurements (Fig. 6) were conducted on CDs, TiO_2 , and hybrid materials. The results for TiO_2 show bands characteristic of the anatase structure. In $\text{TiO}_2(1)$, a broad band with two maximums at 480 and 644 cm^{-1} can be observed, corresponding to the Ti-O bending mode and Ti-O-O stretching mode, respectively.^{48,49} In $\text{TiO}_2(2)$, only one broad band with maximum intensity at 550 cm^{-1} can be observed, which is also assigned to the Ti-O stretching mode.⁵⁰ The differences in location and the number of maximum intensities can arise from variations in sample size, shape, or different sample preparation methods. However, bands in the range of 400–800 cm^{-1} are consistently assigned to Ti-O vibrations.⁵¹ In both types of TiO_2 , the results show peaks at 1634 and 3400 cm^{-1} , representing Ti-O-H and O-H stretching modes, respectively.⁵² Infrared measurements of hybrid materials show results consistent with the Raman spectra, where the bonds from titanium oxide dominate. The results of PhCDs show a very intensive peak at 3223 and 1197 cm^{-1} , assigned to the stretching and bending vibrations of O-H groups, respectively. Additionally, a characteristic peak

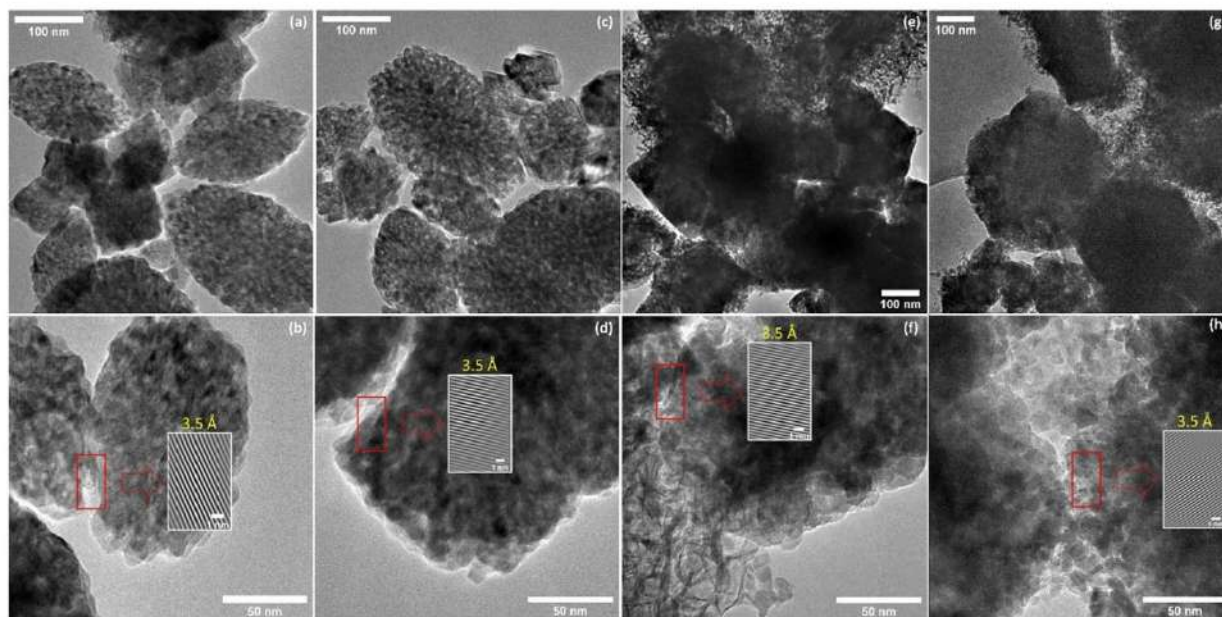


Fig. 3 TEM images of (a and b) CDs@TiO₂(1), (c and d) PhCDs@TiO₂(1), (e and f) CDs@TiO₂(2), and (g and h) PhCDs@TiO₂(2).

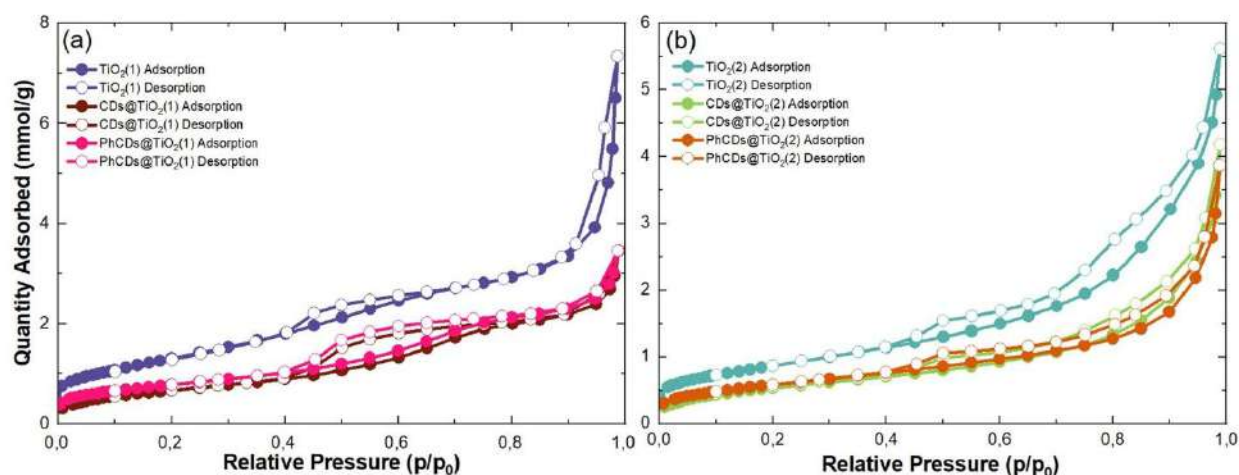


Fig. 4 N₂ adsorption-desorption isotherms (77 K) of raw TiO₂(1) (a) TiO₂(2) (b) and their hybrids.

Table 2 Textural properties of TiO₂ and CDs@TiO₂

Sample	S_{BET} m ² g ⁻¹	V_{total} cm ³ g ⁻¹
TiO ₂ (1)	106	0.12
CDs@TiO ₂ (1)	54	0.08
PhCDs@TiO ₂ (1)	62	0.08
TiO ₂ (2)	68	0.11
CDs@TiO ₂ (2)	42	0.07
PhCDs@TiO ₂ (2)	47	0.06

at 650 cm⁻¹, corresponding to the deformation mode of this bond, can be observed. Another intense peak is present at 1470 cm⁻¹, characteristic of the stretching mode of B–O, along

with a smaller peak at 884 cm⁻¹. Peaks located at 796 and 548 cm⁻¹ represent the deformation and bending modes of B–O, respectively.^{53,54} The CDs structure consists of an aromatic carbon core and different functional groups on the surface, which can be observed in the IR spectra. In the results, peaks assigned to carbon aromatic structures like C–H and C=C can be observed at around 750 and 1500 cm⁻¹ respectively.⁵⁵ On the surface of carbon dots, carbon atoms are connected with oxygen and nitrogen, as seen in the results. The peaks at around 1700, 1300, and 1150 cm⁻¹ are assigned to the C=O,⁵⁶ C–N–C saturated⁵⁷ and C–O⁵⁸ bonds, respectively. The hybrid materials yield similar results, and the characteristic peak of bond Ti–C cannot be observed at about 460 cm⁻¹ (ref. 59)

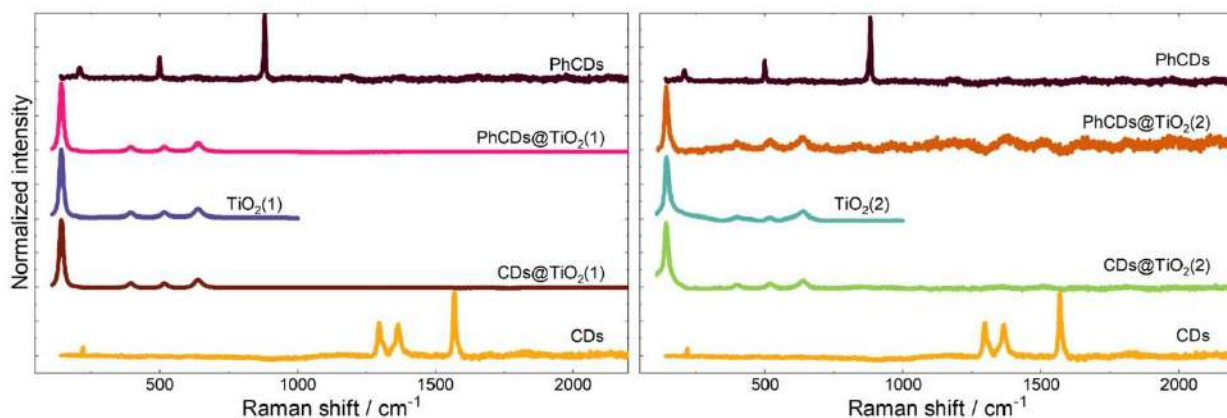


Fig. 5 Raman spectra of CDs, TiO_2 , and hybrid materials.

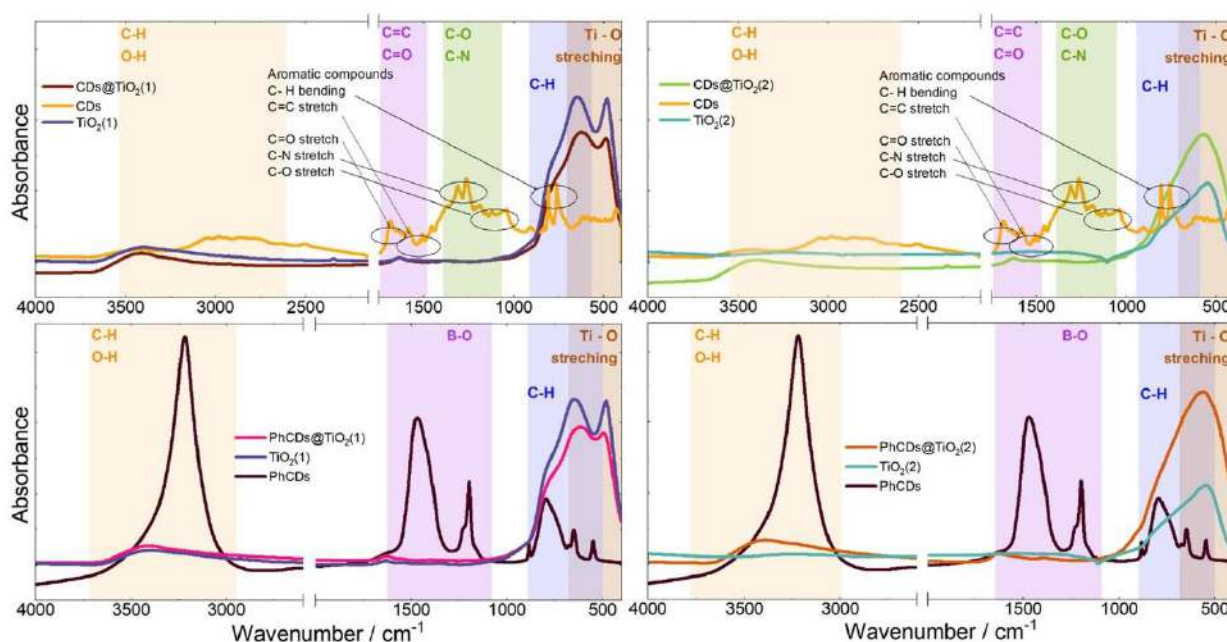


Fig. 6 IR spectra of CDs, TiO_2 , and hybrid materials.

which means that the carbon dots are not connected with TiO_2 by metallic or covalent bonds.

3.2. Spectroscopic properties of CDs@TiO_2

Absorption. The spectra of both TiO_2 samples reveal that these materials absorb UV light very effectively. The absorption edge of $\text{TiO}_2(1)$ occurs at 330–400 nm and of $\text{TiO}_2(2)$ occurs at 330–380 nm. Based on the absorption spectra of $\text{TiO}_2(1)$ and $\text{TiO}_2(2)$, the bandgap energy was calculated using the Kubelka–Munk theory. The energy gap for $\text{TiO}_2(1)$ was 3.364 eV and for $\text{TiO}_2(2)$ 3.322 eV. For other materials, the bandgap was not calculated due to the presence of the carbon dots' absorption band, which blurs the edge of TiO_2 absorption, making it difficult to determine the energy gap. After impreg-

nating $\text{TiO}_2(1)$ with PhCDs, the absorption intensity increases across the entire range compared with pure TiO_2 (Fig. 7). Normalized spectra show that (Fig. S3†) the UV absorption range is wider for $\text{PhCDs@TiO}_2(1)$ than for pure $\text{TiO}_2(1)$, which proves that the addition of PhCDs to $\text{TiO}_2(1)$ shifts the absorption edge to a higher wavelength, allowing for more efficient energy transfer at lower energy. The spectrum for $\text{PhCDs@TiO}_2(2)$ shows an increase in intensity in the UV range, but the absorption edge shifts slightly to a shorter wavelength.

The spectrum of PhCDs (Fig. 7) shows a wide band of absorption from UV to visible light with the highest intensity in the UV range. The maximum absorption at 220 nm is assigned to the p-p* transition of the C=C bond.⁵⁴ The CDs

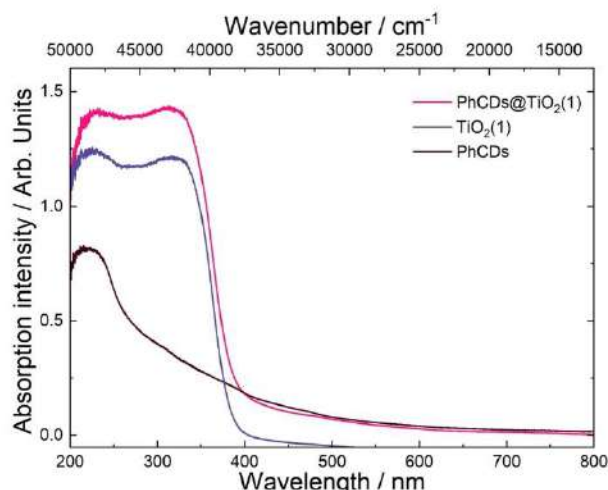


Fig. 7 Absorption spectrum of PhCDs@TiO₂(1), PhCDs and TiO₂(1) compounds.

(Fig. S4†) absorb very well in the UV and blue range, and in the spectrum two separated bands are present, each consisting of two peaks. Absorption peaks at 225 and 253 nm can be also assigned to the p-p* transition of the C=C bond, while peaks at 420 and 444 nm can be attributed to the surface states in which free electron pairs can overlap with n-p* transitions.

The hybrid of CDs@TiO₂(1) shows a significant increase in the absorption intensity in the UV compared with pure TiO₂(1) (Fig. S4†) and also results in a broader absorption range extending from UV to VIS. After the addition of CDs to TiO₂(2) (Fig. S4†), a band assigned to 450 nm of CDs can be seen in the absorption spectrum, proving that CDs are embedded in TiO₂ pores.

Emission. Analysis of the absorption spectra revealed distinct bands for TiO₂ and CDs. Six excitation wavelengths were employed for observation to comprehend the nature of these bands and assess the emission efficiency. We used an excitation wavelength above the CB (320, 350 nm), at the bottom of the CB (370 nm) and below it (390, 420, 450 nm).

TiO₂ exhibited the highest emission intensity in the 350–500 nm range when excited at wavelengths of 320, 350, and 370 nm (Fig. 8 and Fig. S5†). The maximum emission intensity for TiO₂(2) is shifted to the red compared with the TiO₂(1) when the excitation wavelength was 320 or 350 nm. At 390 nm (Fig. S5†) excitation, it was observed that TiO₂(1) emitted effectively in the 400–600 nm range, while TiO₂(2) emitted within the narrower range of 400–500 nm. When the samples were excited by a 420 nm (Fig. 8) or 450 nm (Fig. S5†) wavelength, both types of TiO₂ displayed a similar broad emission band in the 450–800 nm range.

The nature of the emission can be explained by the mechanisms observed for TiO₂. It is based on the presence of oxygen vacancies present in the structure of the material. They occur when an oxygen atom is missing from its designated position in the lattice. This absence can occur due to various reasons, such as structural irregularities within the lattice. For instance, there may be titanium atoms without complete oxygen coordination in certain regions of the lattice, such as at the edges. These vacancies can lead to the creation of free electrons which can migrate to other locations within the lattice, where they may occupy Ti⁴⁺. This process results in the formation of Ti³⁺ and F[•] centers, which are categorized as shallow and deep trap states, respectively. The Ti³⁺ trap is located at 0.51 or 0.8 eV below the CB. The energy gap calculated based on the absorption spectra was 3.37 and 3.34 eV for TiO₂(1) and TiO₂(2), respectively. So shallow traps are located at 2.87 and 2.57 eV in TiO₂(1) and 2.84 and 2.54 eV in TiO₂(2).

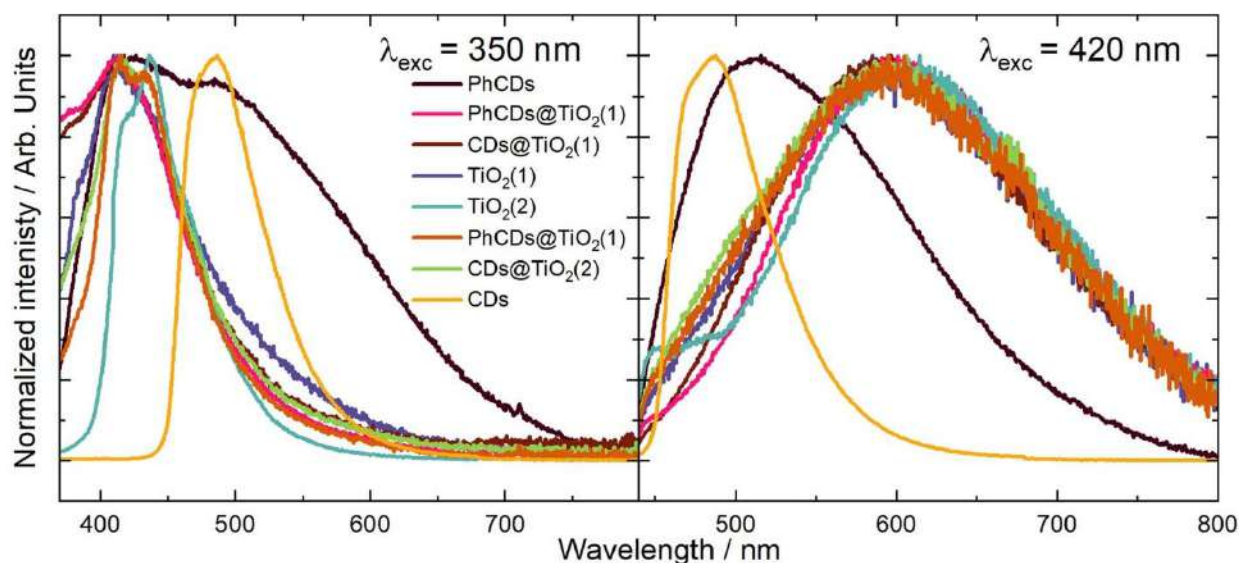


Fig. 8 The emission spectrum of CDs, TiO₂, and hybrid materials under excitation wavelengths of 350 and 420 nm.

To precisely understand the emission mechanism, deconvolution operations were performed to extract the component peaks that constitute the emission band visible in the obtained spectra. The obtained results allowed for a better understanding of the energy structure of materials. Calculations showed that at an excitation wavelength of 350 nm for $\text{TiO}_2(1)$, the emission band consisted of three components corresponding to the energy states of this structure. The most effective emission is observed from states of 3.05 eV, which is visible on the graph as the maximum emission. The second level is at 2.83 eV, and the third is at 2.6 eV, which are close to the theoretical positions of the shallow traps described earlier. Both of these states are visible in the spectrum through a broad tail for wavelengths higher than the emission maximum. In the spectrum of $\text{TiO}_2(2)$, three emission intensity maxima can be seen, corresponding to energy states of 2.99, 2.87 and 2.6 eV. As in the case of $\text{TiO}_2(1)$, the energy values of the second and third traps are close to the theoretical values. The emission in $\text{TiO}_2(2)$ is most intense for the second state. The emission bandwidth of $\text{TiO}_2(1)$ is wider than that of $\text{TiO}_2(2)$, which indicates that the energy states are more separated for the former than for the latter. The energy states isolated based on the deconvolution process showed that the two highest states in $\text{TiO}_2(1)$ are separated more widely than in $\text{TiO}_2(2)$. Because the excitation is more energetic than the bandgap of titanium oxide, electrons are transferred from the VB to above the CB, creating an additional state located just below the CB to which electrons pass non-radiatively. These additional states appear in the emission spectra as the most energetic emissions. At an excitation wavelength of 420 nm, the emission spectra for both TiO_2 appear as a broad band. The deconvolution operation resulted in the separation of two band components, which correspond to two energy states. The distinction between the levels distance in $\text{TiO}_2(1)$ and $\text{TiO}_2(2)$ is similar to that in the previous excitation. The states in $\text{TiO}_2(1)$ are located at 2.2 and 1.9 eV, and for $\text{TiO}_2(2)$ at 2.14 and 1.94 eV. In this case, the amount of energy supplied with the excitation, which corresponds to 2.95 eV, can be considered the energy gap. According to the theory of traps in TiO_2 described above, the traps should

be located 0.51 and 0.8 eV below the energy gap. This means that states with energies of 2.44 and 2.15 eV should be created for this excitation. Only the second trap can be observed in the emission spectra. This means that electrons excited below the CB are trapped in the first defect (~ 2.44 eV) and non-radiatively pass to the second one (~ 2.15 eV), creating an additional virtual energy state of ~ 1.9 eV. Emission occurs in both of these energy states. For this excitation, the difference in bandwidth for $\text{TiO}_2(1)$ and $\text{TiO}_2(2)$ is also visible. The emission band of $\text{TiO}_2(1)$ is much broader than that of $\text{TiO}_2(2)$, which means that the energy difference of the states is also larger. The broader distribution of states in $\text{TiO}_2(1)$ compared with $\text{TiO}_2(2)$ results in more effective electron transfer between levels. In $\text{TiO}_2(2)$, where the energy states are closer, non-radiative transitions may occur more easily. Therefore, the photocatalysis process should be more effective for the first type of titanium dioxide than the second one, which was proved later.

The emission spectra of carbon dots were measured under six excitation wavelengths, the same as in the case of TiO_2 . PhCDs are carbon dots placed in a polycrystalline matrix. The emission in this structure depends on the excitation wavelength, which, according to a leading article, can be attributed to the existence of many triplet excited states in the hybrid (Fig. 8 and Fig. S5†).²⁵ The polycrystalline matrix is responsible for stabilizing the triplet levels in the carbon dots, resulting in a phosphorescence. In these studies, all the spectra (Fig. 8) show a wide emission band. For these types of carbon dot, the emission spectra are based on two factors. The first is fluorescence (FL), during which electrons move from the singlet state to the VB of the carbon dots and emit photons. The second factor is phosphorescence, which involves the transfer of electrons via an intersystem transition (ISC) to the triplet state and then transfer to the VB while emitting photons (Fig. 9). Both of these processes can be observed in the emission spectra as one broad band consisting of a narrow peak corresponding to fluorescence and a broad peak at higher wavelengths corresponding to phosphorescence. It can also be observed that different excitation wavelengths result in differences in the emission spectra. The use of a higher energy exci-

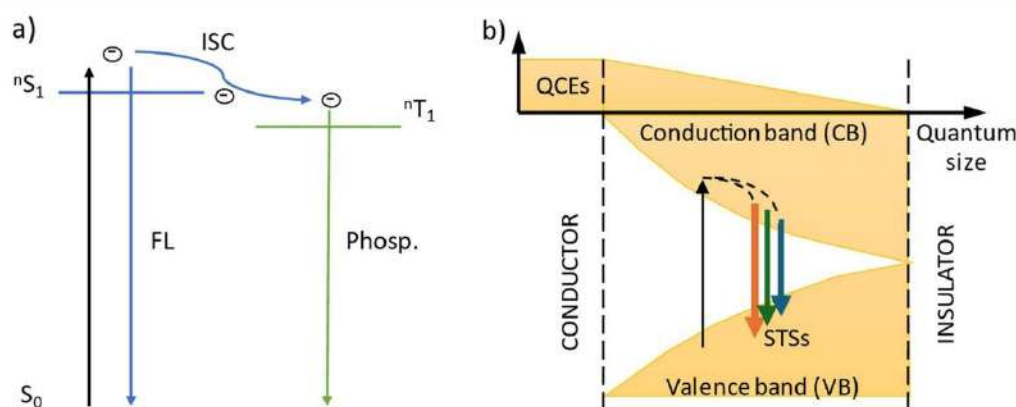


Fig. 9 Scheme of the emission process in (a) PhCDs and (b) CDs.

tation source results in the presence of two maxima in the emission spectra. However, after performing the deconvolution operation, three components of a given band can be isolated. When the excitation has a lower energy, it results in reduced band separation in the spectrum, narrower bands, and the extraction of only two components. This observation leads to the conclusion that lower excitation energy results in fewer electrons transferred through the inter-system transition to the triplet state, and phosphorescence is observed with lower efficiency. As expected, CDs show narrower bands (Fig. 8 and Fig. S5†) because these types of carbon dot only show fluorescence. Therefore, no additional bands resulting from phosphorescence can be observed.

For carbon dots, the emission depends on the quantum confinement effects (QCEs) or surface trap states (STSS) (Fig. 9). The size of the carbon dots influences the width between the CB and VB, and surface defects introduce metastable energy levels in the bandgap. By adjusting this metastable level, it is possible to slightly change the color of the emission in carbon dots of the same size. For these studies, solutions containing a mixture of carbon dots of various sizes and surface functionalizations were used. This diversity of material is visible on the spectrum as a narrow band with a wide base. This band consists of four components, which is confirmed by the presence of carbon dots of different sizes and surface groups. The spectra show that the location of the maximum emission intensity and even the shape of the bands do not depend on the excitation wavelength. This means that CDs always emit photons of the same energy. The only change

when using a different excitation wavelength is the change in emission intensity.

In the case of hybrid materials, the emission spectra have a shape and maximum intensity location similar to the results obtained for pure TiO_2 . This result was expected due to the small amount of carbon dots in the hybrid materials, resulting in a higher response from pure TiO_2 compared with carbon dots. It has been observed that some levels occurring in pure materials are not active in the emission process in hybrids (Fig. 10). Such states were called inactive states. Hybrid materials with $\text{TiO}_2(1)$ show a higher intensity (Fig. S6†) of emission than pure $\text{TiO}_2(1)$. This is because electrons are transferred from inactive states in separate materials to levels from which emission occurs in hybrid materials, causing more radiative transitions to occur in the hybrid than in the titanium dioxide (1). Conversely, opposite results can be observed in hybrid materials with $\text{TiO}_2(2)$ where the intensity of emission is lower than for pure materials (Fig. S7†). This indicates that electrons are transferred from emission states to inactive states, resulting in non-radiative energy loss. What is worth emphasizing is that using 350 nm excitation in the case of $\text{TiO}_2(1)$ hybrids, emission can be observed both from the CB (2) and from defects located in the energy gap (3). In the case of the $\text{TiO}_2(1)$ hybrid, the transfer of electrons from inactive states to emission states results in an additional influx of electrons that can be used for the photocatalysis process (Fig. 10). If the electrons occupying the energy levels are used for photocatalysis, supplementary electrons from the carbon dots become available. Conversely, in $\text{TiO}_2(2)$ hybrids (Fig. S8†),

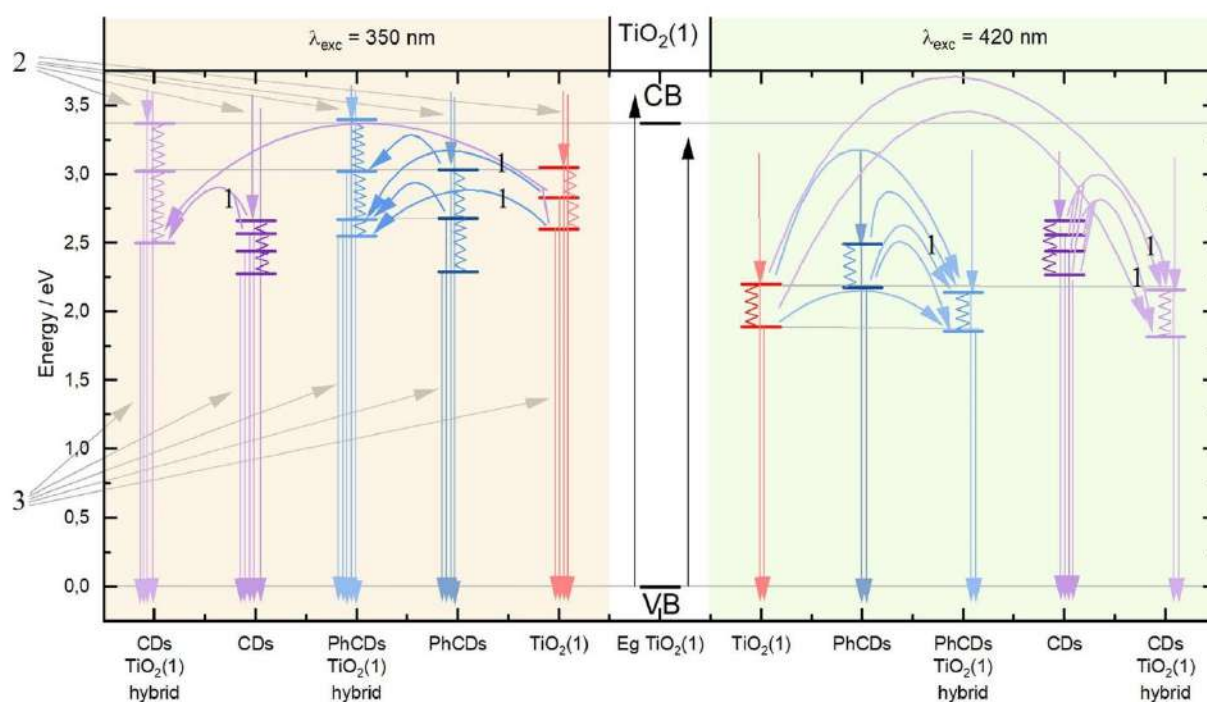


Fig. 10 Mechanism of energy transfer in $\text{TiO}_2(1)$, PhCDs, CDs, and hybrid materials.

electron transfer occurs from the hybrids to states within carbon dots where electron energy is dissipated non-radiatively (4). These electrons are not utilized as a substitute for others involved in photocatalysis.

Luminescence kinetics. Luminescence kinetics measurements of PhCDs, CDs, $\text{TiO}_2(1)$, $\text{TiO}_2(2)$, and their hybrids were carried out with excitation wavelengths of 350 and 390 nm. For each result, the wavelength at which the maximum emission occurred was determined. The lifetimes of each material were then calculated for the maximum emission values of the starting materials and their hybrids (Table 3).

At 350 nm excitation, the maximum emission occurred at wavelengths of 440 and 480 nm for PhCDs, 520 nm for $\text{TiO}_2(2)$, and 500 nm for their hybrid. Therefore, to compare the lifetimes of these materials, calculations were performed for all four wavelengths (440, 480, 500, and 520 nm). For CDs, maximum emission values occurred at wavelengths of 470 and 485 nm, and for the $\text{CDs@TiO}_2(2)$ hybrids at 490 nm. Consequently, lifetimes for dots, $\text{TiO}_2(2)$, and hybrids were calculated for four wavelengths (470, 485, 490, and 520 nm). For excitation at 390 nm, PhCDs had maximum emission at 470 nm, $\text{TiO}_2(1)$ at 460 nm, and the hybrid, like PhCDs, at 470 nm. Thus, lifetimes for these materials were calculated for two wavelengths (460 and 470 nm).

Based on the obtained luminescence kinetics measurements, it can be concluded that for the 350 nm excitation, the lifetime of electrons in $\text{TiO}_2(2)$ in the excited state is approximately 3.3 ns. When excited with a higher wavelength of 390 nm, the lifetime of electrons in $\text{TiO}_2(1)$ is shorter, at approximately 2.7 ns.

The lifetime of electrons in PhCDs emitting in the range of 440–520 nm depends on the maximum emission value for which they were measured. For lower wavelengths, the lifetime is shorter, around 10 ns, and increases to 14 ns as the emission wavelength increases. This is expected due to the phosphorescence properties of these dots. As described in the emission spectra analysis, the emission shortly after excitation is responsible for the maximum emission at shorter wavelengths. However, the tail in the emission spectrum at longer wavelengths reflects phosphorescence, where electrons are held for a period before relaxing, accounting for their longer lifetime.

For the 390 nm excitation, where the measured times were for closely located maxima, the lifetime was 16.5–17 ns, indicating that with lower energy excitation, electrons remain in the excited state longer.

CDs excited at a wavelength of 350 nm emit in a narrow range which is in alignment with the maximum wavelengths determined during luminescence kinetics measurements. This means that in these dots, electron relaxation occurs shortly after excitation without additional storage. Electron lifetimes in the emission range of 470–520 nm were similar, around 12.7 ns.

The addition of PhCDs/CDs to $\text{TiO}_2(2)$ significantly reduced electron lifetimes compared with pure $\text{TiO}_2(2)$. The addition of PhCDs nearly halved the lifetime. In the hybrid, electrons have a lifetime of about 1.8 ns. Notably, for the $\text{PhCDs@TiO}_2(2)$ hybrid, the lifetimes for various maximum emissions were similar, unlike in pure PhCDs. For CDs, whose lifetime did not depend on the emission wavelength, their addition to $\text{TiO}_2(2)$ resulted in a hybrid material with electrons of different lifetimes. Electrons in $\text{CDs@TiO}_2(2)$ have the longest lifetime of 2.6 ns for the shortest emission wavelength, decreasing to 2.38 ns as the wavelength increases. For $\text{TiO}_2(1)$, adding PhCDs almost tripled the lifetimes (6.39 and 6.56 ns). The lifetime extension indicates the positive impact of adding PhCDs to the photocatalyst on the photocatalysis process. A longer lifetime means a slower recombination of electron–hole pairs, increasing the efficiency of the photocatalytic process.

The measurements were conducted to compare the decay times of CDs, PhCDs, TiO_2 , and their respective hybrids. All measurements were taken at specific emission wavelengths that excluded the phosphorescence emission maximum (observed at about 560 nm), and therefore, the resulting decay times are not fully representative of this process. To investigate the phosphorescence phenomenon in more detail, an additional experiment was performed. Emission spectra of PhCDs were collected under UV irradiation and at 100 ms intervals after ceasing excitation (Fig. 11a). The spectra were recorded over a broader wavelength range (300–700 nm) to capture phosphorescence, which exhibits a maximum at approximately 560 nm (Fig. 11a). It was observed that the phosphorescence maximum is red-shifted relative to the fluo-

Table 3 Luminescence lifetime for PhCDs, CDs, $\text{TiO}_2(1)$, $\text{TiO}_2(2)$, and their hybrids for 350 and 390 nm excitation

Sample		$\text{TiO}_2(1)$	$\text{TiO}_2(2)$	CDs	$\text{CDs@TiO}_2(2)$	PhCDs	$\text{PhCDs@TiO}_2(1)$	$\text{PhCDs@TiO}_2(2)$
λ_{exc} (nm)	λ_{em} (nm)	τ (ns)						
350	440	—	3.29	—	—	10.2	—	1.81
	470	—	3.31	12.5	2.6	—	—	—
	480	—	3.33	—	—	12.1	—	1.77
	485	—	3.31	12.7	2.51	—	—	—
	490	—	3.37	12.7	2.46	—	—	—
	500	—	3.42	—	—	13.3	—	1.72
	520	—	3.47	12.6	2.38	14.1	—	1.76
390	460	2.68	—	—	—	16.5	6.39	—
	470	2.70	—	—	—	17.1	6.56	—

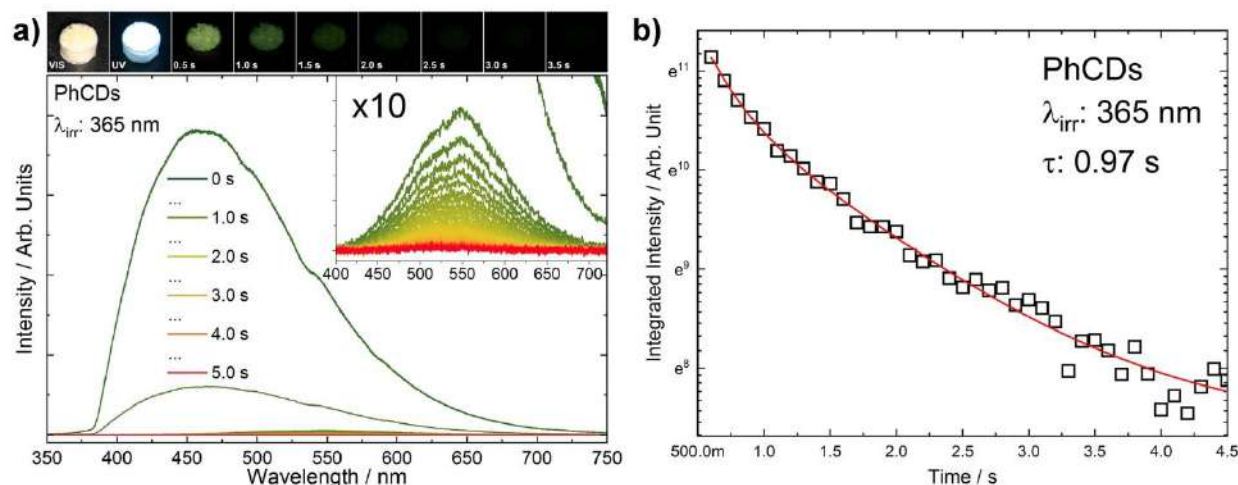


Fig. 11 (a) PhCDs luminescence spectrum as a function of time (the inset shows the enlarged range in which phosphorescence is observed). Above the graph, PhCDs photos are presented under VIS and UV irradiation, and after UV ceasing with a step of 0.5 s. (b) The decay of PhCDs phosphorescence.

rescence emission (inset in Fig. 11a). From the recorded spectra, the decay of phosphorescence was calculated (Fig. 11b) to be approximately 970 ms, which is consistent

with the characteristic behavior of the phosphorescence process and is consistent with the data presented in the source article on which the synthesis was based, as well as with results obtained by other research groups (Table 4).

Table 4 Comparison of the luminescence decay times of phosphorescent carbon dots

Sample name	Decay times (ms)	Ref.
PhCDs	970	Present work
CDC ₄₀₀ ¹⁸⁰	582 ^a	31
CD in silica gel	840	60
CD_CA in water	687	61
NCDs	1060	62
a-CDs/BA	1600	63
ACD/PVA	450	64

^a Average value.

3.3. Photocatalytic activity

The photocatalytic activity of the prepared materials was evaluated based on the degradation process of carbamazepine, a pharmaceutical commonly detected in water that is non-susceptible to biodegradation. As can be seen in Fig. 12, TiO₂(1) showed improved photocatalytic activity compared with the reaction of CBZ degradation using TiO₂(2). For TiO₂(1), the removal efficiency reached nearly 96% within 60 min of irradiation under simulated solar light. Furthermore, for this material, the reduction of total organic carbon (TOC) was 51%, which indicates the potential for efficient photodegradation

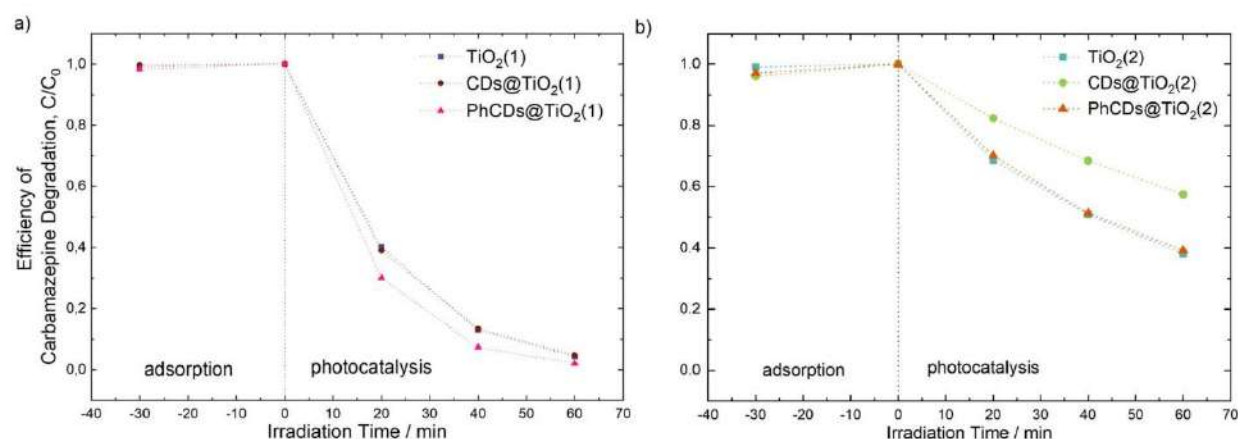


Fig. 12 Efficiency of carbamazepine degradation for (a) pure TiO₂(1) and hybrid materials PhCDs@TiO₂(1) and CDs@TiO₂(1), and (b) pure TiO₂(2) and hybrid materials PhCDs@TiO₂(2) and CDs@TiO₂(2).

and mineralization of persistent organic pollutants. The enhanced photocatalytic activity may be correlated with the larger surface area of the $\text{TiO}_2(1)$ ($106 \text{ m}^2 \text{ g}^{-1}$) photocatalyst than that of $\text{TiO}_2(2)$ ($68 \text{ m}^2 \text{ g}^{-1}$). Generally, a photocatalyst with a higher surface area possesses more reactive sites and is characterized by a shorter migration distance; therefore, the recombination rate may be reduced. For $\text{TiO}_2(1)$, modification of the surface with CDs did not affect the CBZ degradation efficiency. However, in the case of $\text{TiO}_2(1)$ modified with PhCDs, enhancement in the photocatalytic activity was observed. The CBZ degradation rate constant increased from $5.31 \times 10^{-2} \text{ min}^{-1}$ to $6.59 \times 10^{-2} \text{ min}^{-1}$, and TOC removal increased to 60%. The opposite effect was observed for $\text{TiO}_2(2)$, where the modification of the TiO_2 surface was not accompanied by an improvement in the photocatalytic activity. In particular, the presence of luminescent carbon dots caused a decrease in the degradation efficiency. Moreover, none of these samples showed the ability to mineralize organic pollutant (Table 5).

The above results and the results obtained from emission and lifetime measurements show a correlation between the efficiency of photocatalytic activity and the energy transfer mechanism. The addition of PhCDs and CDs to $\text{TiO}_2(1)$ resulted in an increase in emission intensity, which was explained as the non-radiative electron transfer between the

excited states of TiO_2 and CDs to the valence band and participating in the luminescence observed in the hybrid. During photocatalysis these electrons take part in the production of radicals that participate in the decomposition of pollutants. The phosphorescence phenomenon occurring in PhCDs helps to slow down the recombination of the charges due to trapping electrons and participation of the holes in the generation of radicals, also involved in the degradation of carbamazepine. The addition of PhCDs to $\text{TiO}_2(1)$ resulted in a prolonging of the hybrid luminescence lifetime compared with pure $\text{TiO}_2(1)$, which confirms the positive effect of this combination. Due to this process, an improvement in the PhCDs@ $\text{TiO}_2(1)$ photocatalysis process can be observed. In the case of $\text{TiO}_2(2)$ hybrids, CDs/PhCDs are located in large amounts on the surface of the photocatalyst, not in its pores. Based on the emission spectra, it was found that the electron transfer is reverse. Electrons move from hybrid states to states in carbon dots, where non-radiative transitions occur. This results in a limited number of electrons that can take part in the formation of radicals. Also in the lifetime measurements, a negative effect of the addition of carbon dots to $\text{TiO}_2(2)$ could be noticed. This is the reason why a decrease in photocatalysis efficiency is observed in the case of $\text{TiO}_2(2)$ hybrids.

Additional experiments were conducted for the PhCDs@ $\text{TiO}_2(1)$ sample exhibiting the highest photocatalytic activity in the degradation of CBZ under UV-vis irradiation. As illustrated in Fig. 13a and Table 6, even a two- and four-fold reduction in the photocatalyst concentration within the reaction medium facilitated a high degradation efficiency. The optimal photocatalyst concentration was determined as 1 g dm^{-3} . In the case of 2 g dm^{-3} , the increased turbidity may have resulted in light scattering and screening effects, consequently decreasing the photocatalyst activation. The effect of the CBZ solution concentration on the photocatalytic activity was also investigated. As shown in Fig. 13b and Table 6, a decrease in the CBZ concentration to 8.5 mg dm^{-3} resulted in an increase in the degradation rate constant from 7.33×10^{-2}

Table 5 Photocatalytic activity of the prepared samples

Sample name	Carbamazepine degradation efficiency, %	Degradation rate constant $k \times 10^{-2}, \text{ min}^{-1}$	Efficiency of TOC reduction, %
$\text{TiO}_2(1)$	95.8	5.31	50.7
CDs@ $\text{TiO}_2(1)$	95.3	5.11	2.4
PhCDs@ $\text{TiO}_2(1)$	98.0	6.59	60.2
$\text{TiO}_2(2)$	61.8	1.60	0
CDs@ $\text{TiO}_2(2)$	42.6	0.93	0
PhCDs@ $\text{TiO}_2(2)$	60.8	1.56	0

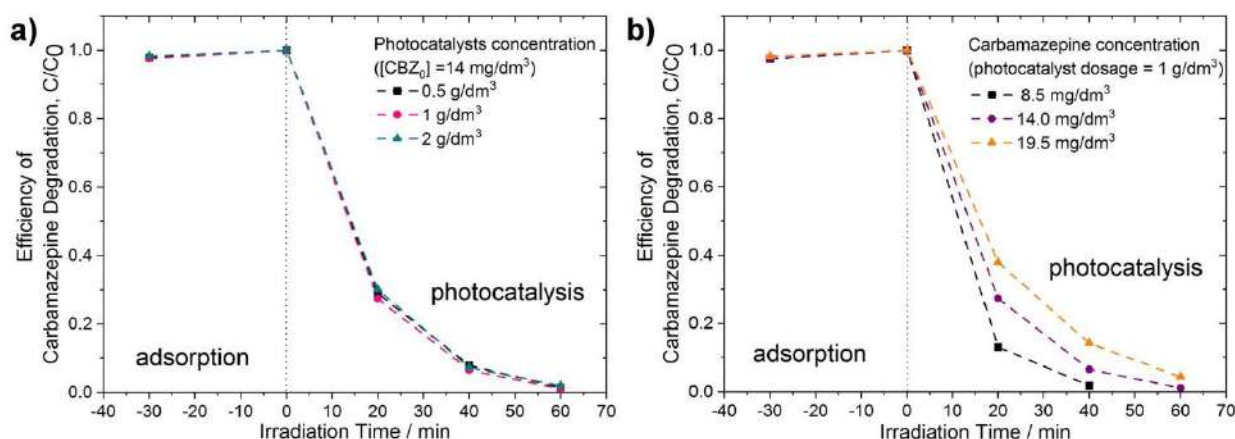


Fig. 13 Efficiency of carbamazepine degradation (a) at various dosages of PhCDs@ $\text{TiO}_2(1)$ photocatalyst, $[\text{CBZ}_0] = 14 \text{ mg dm}^{-3}$, and (b) using PhCDs@ $\text{TiO}_2(1)$ photocatalyst at various concentrations of CBZ solution, photocatalyst dosage = 1 g dm^{-3} .

Table 6 Photocatalytic activity of the PhCDs@TiO₂(1) photocatalyst applied at various dosages, [CBZ]₀ = 14 mg dm⁻³ (yellow), and at various concentrations of CBZ solution, photocatalyst dosage = 1 g dm⁻³ (green)

Dosage of		Degradation rate constant $k \times 10^{-2} \text{ (min}^{-1}\text{)}$	Efficiency of TOC reduction (%)
photocatalyst (g dm ⁻³)	CBZ (mg dm ⁻³)		
0.5	14	7.01	63.1
1	14	7.33	61.9
2	14	6.59	60.2
1	8.5	9.94	67.0
1	14	7.33	61.9
1	19.5	5.22	65.6

min⁻¹ to $9.94 \times 10^{-2} \text{ min}^{-1}$. Almost complete degradation was observed within 40 min of irradiation. Conversely, increasing the CBZ concentration to 19.5 mg dm⁻³ produced the opposite effect: the degradation rate constant decreased to $5.22 \times 10^{-2} \text{ min}^{-1}$. When the concentration of the pollutant increases, the number of intermediates, which may compete for active sites because of the non-selective nature of the photocatalytic process, also increases. This may have led to a decrease in the overall degradation rate.⁶⁵ Additionally, higher initial concentrations cause the pollutant to occupy more active sites, thereby hindering the production of oxidants. Furthermore, higher initial CBZ concentrations lead to greater photon absorption. As a result, fewer photons are available to activate the photocatalyst, causing diminished photocatalytic activity because the catalyst surface becomes inactive.⁶⁶

To identify the primary reactive species involved in the carbamazepine degradation process under UV-vis light using PhCDs@TiO₂(1) photocatalyst, trapping experiments were conducted in the presence of scavengers. As illustrated in Fig. 14, the most significant inhibition of CBZ degradation was observed following the addition of ascorbic acid. In this

instance, the degradation efficiency decreased to approximately 25% within 60 minutes of irradiation, indicating that superoxide anion radicals play a crucial role in CBZ removal. Furthermore, [•]OH and ¹O₂ may also be attributed a significant role in the degradation process. The addition of *tert*-butanol and sodium azide resulted in a reduction of photocatalytic activity, with 57% and 67% degradation within 60 minutes, respectively. Upon the addition of ammonium oxalate, a scavenger of h⁺, the degradation efficiency decreased to 93%, indicating that these species have a minor contribution to the reaction pathway of CBZ.

4. Conclusions

The investigated hybrid materials consisted of titanium oxide impregnated with carbon dots. Four hybrids were created consisting of two types of TiO₂ and two types of carbon dot. Structural tests showed no changes in the structure of TiO₂ after the addition of carbon dots, which was confirmed by SEM, TEM and BET analysis. In Raman and IR spectroscopy, no significant differences were observed between the hybrid materials and pure titanium oxide due to the small number of CDs. Absorption measurements showed that adding CDs to TiO₂(1) causes the absorption edge to shift towards visible light and increases the absorption intensity across the entire range for all hybrids. Analysing the emission spectra of the raw and hybrid materials allowed for understanding the mechanism of luminescence in hybrid materials. It has been shown that in the case of TiO₂(1), adding carbon dots increases the emission intensity. This means that emission in hybrid materials occurs from the electrons of TiO₂ and carbon dots which enhance the photocatalytic process. In the case of TiO₂(2), the opposite relationship was observed, namely, the addition of carbon dots to titanium oxide resulted in a reduction in emission intensity. The location of CDs mostly on the TiO₂ surface probably leads to non-radiative electron energy loss, which negatively impacts the photocatalysis process. Photocatalytic activity tests confirm this thesis. Thus, in the case of TiO₂(1), the addition of phosphorescent dots improved the photocatalytic process. The optimal photocatalyst concentration was determined as 1 g dm⁻³. The addition of CDs to this type of titanium oxide did not cause major differences in this process. In the case of TiO₂(2), the addition of both types of carbon dot resulted in a reduction in the efficiency of this process.

To summarize, the thesis regarding the improvement of the photocatalysis process by adding phosphorescent carbon dots to titanium oxide has been confirmed. Additionally, it was found that the type of titanium oxide and the properties of the carbon dots have a significant impact on the photocatalysis process. It has been proved that to improve this process, it is important to create a material that can hold electrons in the excited state. This will slow down the recombination of electron-hole pairs, which has a significant impact on the photocatalysis process.

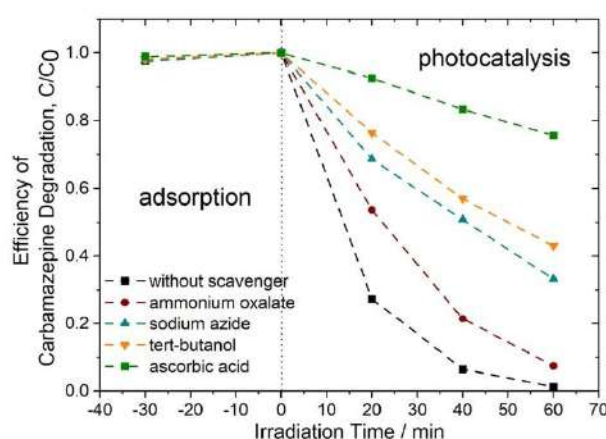


Fig. 14 Efficiency of carbamazepine degradation of PhCDs@TiO₂(1) photocatalyst in the presence of scavengers, [CBZ]₀ = 14 mg dm⁻³, photocatalyst dosage = 1 g dm⁻³.

Data availability

Data for this article, including raw data are available at Zenodo at <https://doi.org/10.5281/zenodo.13832245>.

Conflicts of interest

There are no conflicts to declare.

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Supplementary information

Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst

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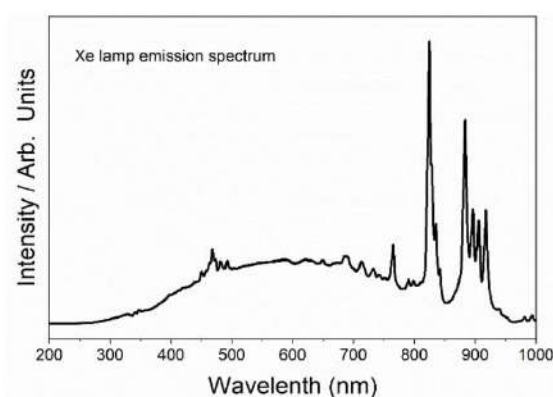


Figure S1. The emission spectrum of the Xe lamp

Table S1. The parameters of the HPLC analysis

Parameter	Value
Wavelength	285 nm
Retention time	4.6 min
Temperature	45 °C
Flow rate	1.5 cm ³ ·min ⁻¹
Mobile phase composition	39.5% acetonitrile, 60% water, and 0.5% orthophosphoric acid



Fig. S2. The image of TiO₂(1), PhCDs and their hybrid compound.

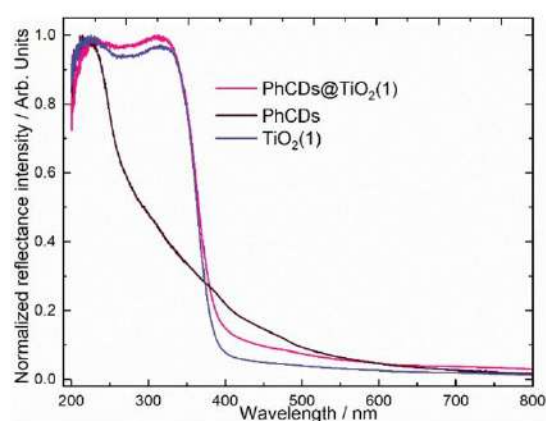


Fig. S3. Normalized absorption spectra of PhCDs@TiO₂(1), PhCDs and TiO₂(1) compounds

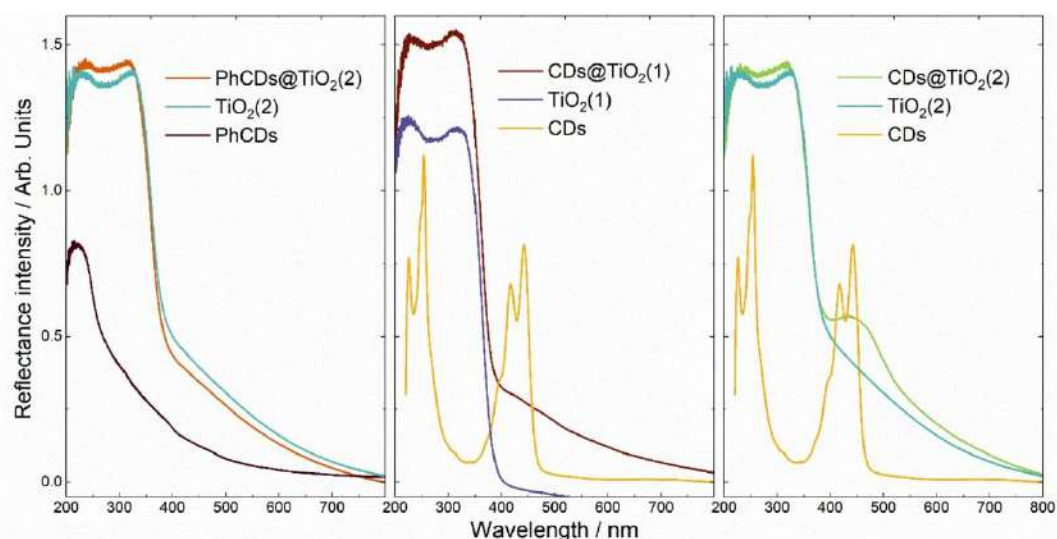


Fig. S4. Absorption spectra of CDs, PhCDs, TiO₂(1), TiO₂(2) and their hybrid compounds.

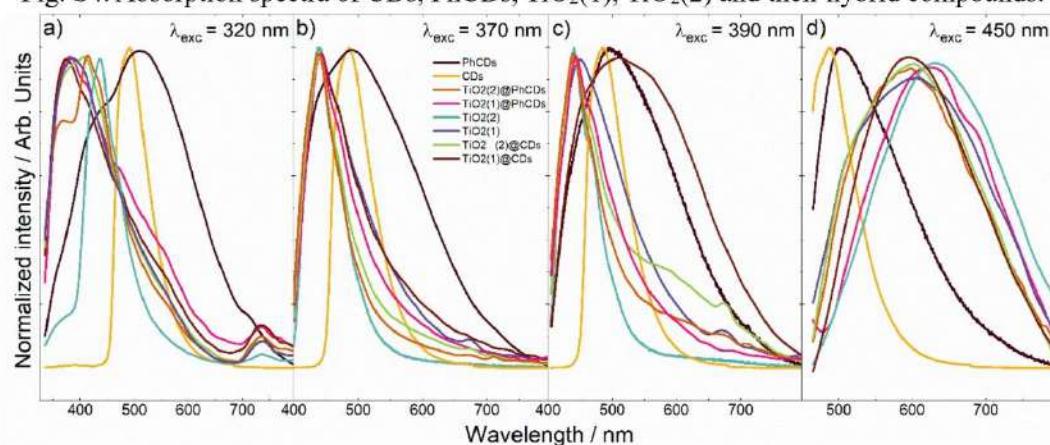


Fig. S5. Normalized emission spectra of CDs, TiO₂ and hybrid materials under excitation wavelength: a) 320 nm, b) 370 nm, c) 390 nm, d) 450 nm

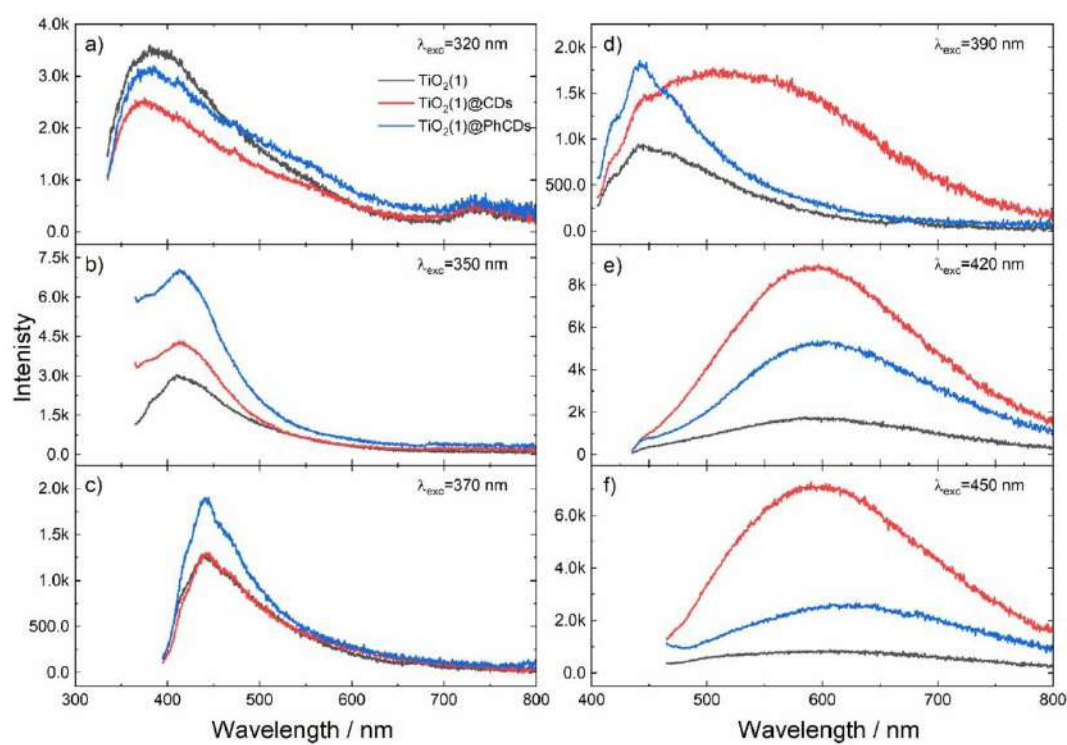


Fig. S6. Emission spectra of $\text{TiO}_2(1)$ and hybrid materials under excitation wavelength a), 320nm, b) 350 nm, c) 370 nm, d) 390 nm, e) 420 nm, f) 450 nm.

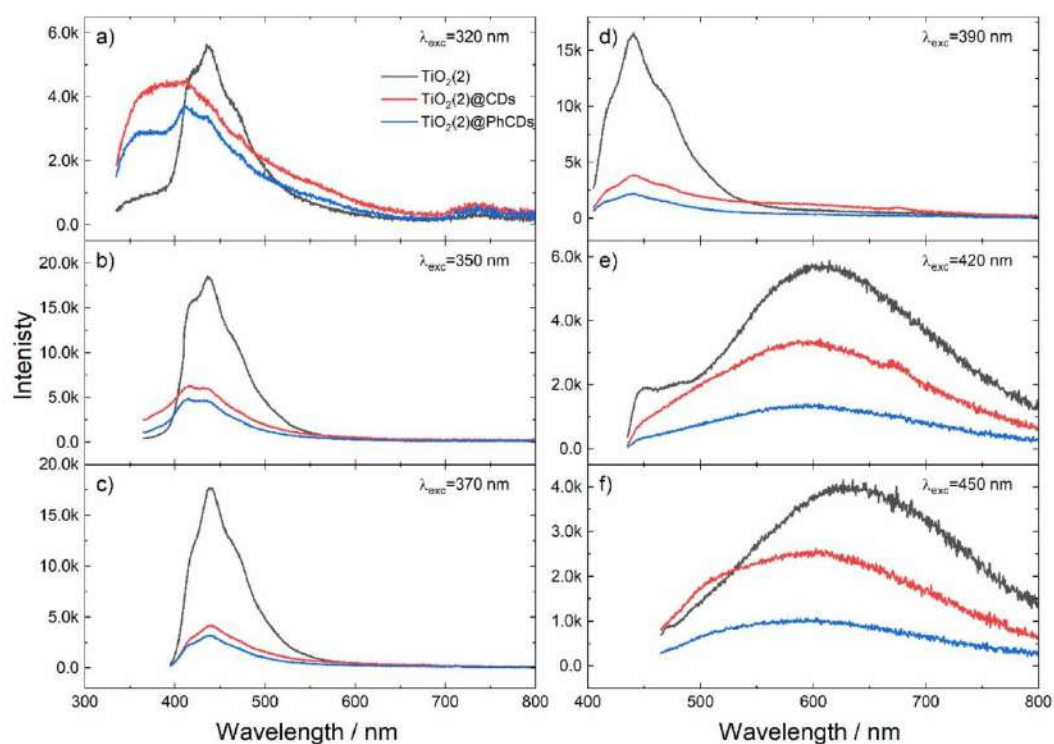


Fig. S7. Emission spectra of $\text{TiO}_2(2)$ and hybrid materials under excitation wavelength a), 320nm, b) 350 nm, c) 370 nm, d) 390 nm, e) 420 nm, f) 450 nm.

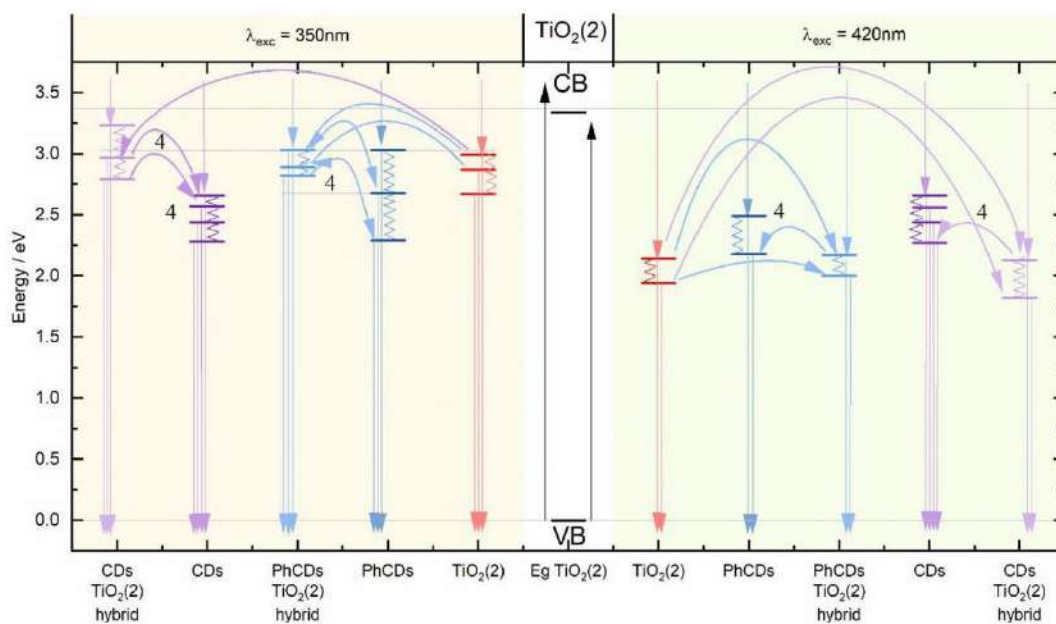


Fig. S8. Scheme of emission mechanism in $\text{TiO}_2(2)$, PhCDs, CDs and hybrid materials.

8.2. Manuscript ready for submission

8.2.1. Interfacial Engineering of CDs@ZnO Hybrids Toward Oxidative and Reductive Photocatalytic Activity under Visible Light (Manuscript ready for submission)

The P4 publication expands on prior research on CDs and their applications in hybrid materials with wide bandgap semiconductors, focusing on precise control of redox properties. The main research goal of this work was to obtain advanced CDs@ZnO hybrid materials and determine how diverse interfacial engineering pathways influence the direction of photocatalytic processes toward oxidation or reduction. This modification aimed to address two key challenges hindering the widespread use of pure ZnO: its wide bandgap, which limits photocatalyst activation to the UV range, and the rapid recombination of photogenerated electron-hole pairs. The system's performance was verified using NPX as a representative pharmaceutical organic contaminant, which is frequently detected in aqueous environments and may be poorly removed by conventional water purification processes.

The P4 publication presents a detailed analysis of five methods for modifying ZnO surfaces with CDs.

- Impregnation (IMP) – conducted at room temperature, where CD deposition is based on weak physical interactions, which ultimately leads to partial pore blocking and a decrease in specific surface area.
- Hydrothermal impregnation (IMP_H) – utilizing elevated temperature and pressure conditions that induced the disintegration of ZnO aggregates, resulting in a more than two-fold increase in specific surface area and the greatest shrinkage of the unit cell, confirming the strong incorporation of CDs into the oxide structure.
- Chemical modification using APTES and impregnation (A_IMP) – the use of (3-aminopropyl)triethoxysilane as a molecular linker at room temperature, allowing for the covalent bonding of dots on the semiconductor surface.
- Chemical modification using APTES and hydrothermal impregnation (A_IMP_H) – combining the action of a silicate linker with pressure-temperature

treatment. This led to the formation of a continuous, densely dotted hybrid organosilica shell, forming a stable structure.

- Electrostatic adsorption (ADS_E) - The acquisition of a positive charge on the ZnO surface by controlling pH, which enabled bonding with negatively charged groups on the CDs surface. This process induced reorganization of the matrix surface, leading to the selective growth of crystalline structures with an elongated, finger-like morphology.

XRD analysis confirmed the preservation of the pure crystalline wurtzite phase in all samples. However, shifts in the diffraction patterns toward higher 2θ angles were observed, caused by lattice contraction induced by the consumption of ZnO surface oxygen groups during the formation of strong interfacial bonds with the CDs.

UV-Vis spectroscopic studies showed that the introduced carbon phase generates a broad, intense absorption band in the visible range (400-600 nm) without altering the ZnO band gap. The intensity of this absorption is closely dependent on the synthesis method, reaching the highest values for the ADS_E sample and the lowest for the APTES-modified samples. Excitation spectra measurements revealed that the A_IMP sample most effectively retains the original electronic CDs, indicating dominance of excitation channels in the visible.

This work proposes a comprehensive charge carrier transfer mechanism that operates under both UV and visible light. The luminescence quenching phenomenon and the prolonged emission decay kinetics clearly confirmed the effective spatial separation of charges and the passivation of deep defect states in the oxide by CDs.

The most important application conclusion from the P4 publication is the demonstration that the choice of surface engineering strategy allows for the selective promotion of specific ROS species (Fig. 12):

- Reduction pathway - the IMP_H sample proved to be a highly optimized reduction photocatalyst. It demonstrated nearly fourfold higher efficiency in generating H_2O_2 under UV-Visible light than pure ZnO, which correlated with intense $\text{O}_2^{\bullet-}$ production. Hydrothermal conditions improved interfacial contact, creating specific active sites for the two-electron pathway of molecular oxygen reduction.

- Oxidation pathway - the APTES-modified samples (A_IMP and A_IMP_H) demonstrated the highest efficiency in generating $\bullet\text{OH}$ radicals across the full UV-Vis spectrum. CDs in this system act as efficient charge transfer agents, opening alternative pathways for water oxidation to $\bullet\text{OH}$ radicals.

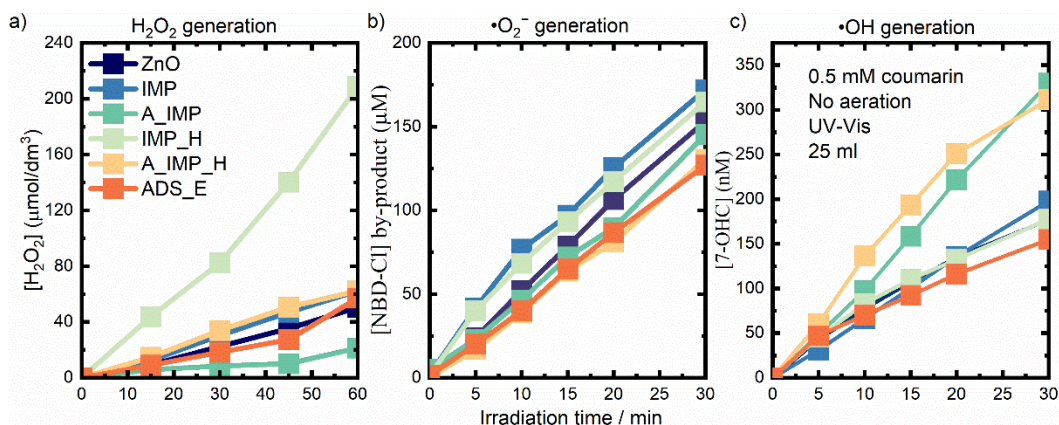


Figure 12. Efficiency of ROS generation under UV-Vis irradiation by pure ZnO and CDs@ZnO hybrid materials.

In NPX degradation tests under visible light, where pure ZnO is practically inactive, samples IMP_H and A_IMP_H achieved the highest efficiency, degrading 54% and 51% of the drug, respectively, within 60 minutes (Fig. 13). The work also includes an analysis of the degree of mineralization. It was demonstrated that the presence of CDs and APTES introduces competitive ROS consumption and autophotodegradation of the carbon phase in the hybrid system, thereby limiting full mineralization of the NPX relative to pure ZnO. However, the use of hydrothermal treatment in sample A_IMP_H yielded the best result of the entire series of hybrid materials.

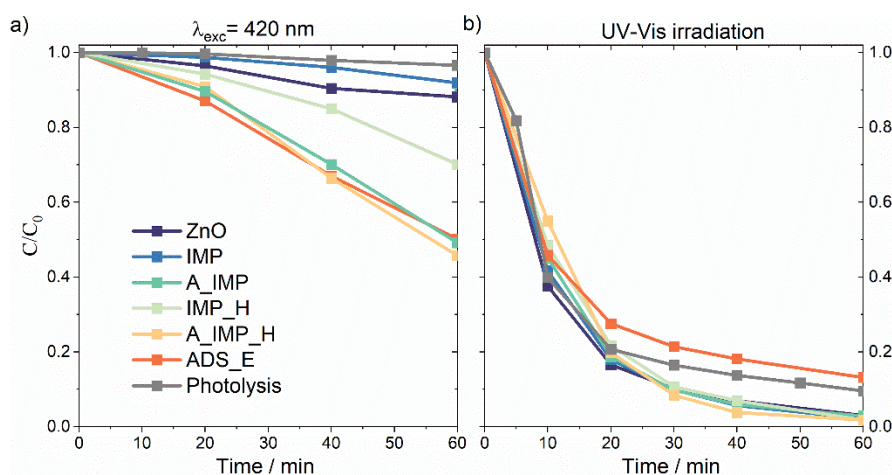


Figure 13. Efficiency of naproxen degradation under a) 420 nm and b) UV-Vis irradiation

The P4 publication represents an important step in the methodology for designing semiconductor-carbon dot nanocomposites. The research demonstrates that the role of CDs is not limited to simply extending the matrix's optical response in the visible or passivating defects. Through the precise architecture of the interfacial junctions, the photocatalyst's desired redox reactivity profile can be deliberately programmed to suit specific degradation processes or chemical syntheses.

Author contribution to the publication P4

conceptualization, planning material impregnation methods, conducting chemical synthesis, preparing hybrid materials, preparing materials for structural and morphological studies, conducting spectroscopic measurements, data processing and preparing their graphic visualization, analyzing the results, planning the manuscript structure, proposing the energy transfer mechanism, preparing the initial and final versions of the manuscript, archiving data after preparation of the final article

CDs@ZnO Photocatalysts with Interfacial-Dependent Oxidative and Reductive Activity

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Abstract:

Zinc oxide (ZnO) is a semiconductor used for photocatalytic applications, but its widespread use is limited by its wide band gap and rapid charge carrier recombination. This work presents the design of advanced carbon dots (CDs) and ZnO hybrid materials, CDs@ZnO, aimed at extending light absorption into the visible spectrum and enhancing the photodegradation of the pharmaceutical contaminant naproxen. Various interfacial engineering strategies were investigated: modification of ZnO with APTES to enhance CDs-ZnO bonding, simple and hydrothermal impregnation of pure and APTES-modified ZnO, and pH-controlled electrostatic adsorption. X-ray diffraction and FTIR analyses confirmed the structural integrity of the wurtzite-structured ZnO matrix and lattice contraction in the hybrid materials. This confirms the strong interfacial bonding occurring through the consumption of surface oxygen groups on CDs. Morphological analysis revealed that combining APTES with hydrothermal treatment formed a shell on the ZnO surface, and electrostatic adsorption caused the surface to reorganize into "finger-shaped" crystalline protrusions. Spectroscopic measurements revealed that while the optical band gap of ZnO remained unchanged, the introduced CDs exhibited broad, intense visible light absorption and created highly efficient, low energy excitation channels. Photoluminescence quenching and prolonged decay kinetics clearly indicated improved charge separation and passivation of deep defect states. As a result, the optimized heterostructures enhanced the visible-light activity, achieving 54% naproxen degradation after 60 min. Additionally, hydrothermally prepared samples showed an 86% increase in hydroxyl radical generation under UV-vis light compared to unmodified ZnO. These

observations are an important pillar for further development of CDs-semiconductor hybrid material design and interfacial tailoring to achieve high-performance visible light photocatalysts.

Keywords: zinc oxide, carbon dots, interfacial engineering, photocatalysis, ROS generation

1. Introduction

Heterogeneous photocatalysis has been widely recognized as an innovative solar-driven technology with promising application prospects in various disciplines, such as chemical synthesis, energy conversion, and water purification^{1,2}. Upon irradiation, a photocatalyst generates electron-hole pairs, which can subsequently drive redox reactions at the photocatalyst surface, producing reactive oxygen species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\text{O}_2^{\bullet-}$) and hydrogen peroxide (H_2O_2). Among the various oxides used in photocatalysis, zinc oxide (ZnO) became one of the most intensively studied semiconductors used as photocatalysts due to its abundance, facile synthesis, and high electron mobility³. Its use in organic pollutant removal processes dates to the beginnings of photocatalysis research in the second half of the 20th century. Despite its numerous advantages, ZnO exhibits limitations that hinder its widespread application. First, due to its wide band gap of approximately 3.3 eV, ZnO is primarily activated by UV light. As UV radiation corresponds to only about 4-5% of the sunlight spectrum, this considerably limits the practical application of this material under solar-light-driven conditions^{4,5}. Moreover, the high electron-hole pair recombination rate lead to low quantum yield and reduced photocatalytic activity. Therefore, surface modification is usually aimed at improving overall photocatalytic performance by enhancing light absorption, improving charge separation efficiency and suppressing recombination of photogenerated charge carriers⁴⁻⁷.

However, higher photocatalytic activity does not necessarily imply an equal improvement in all reaction pathways. Since photocatalytic processes are governed by the availability and redox potential of photogenerated charge carriers, material modification may preferentially promote either reduction- or oxidation-driven reactions. Therefore, the possibility of selectively directing photocatalytic processes toward specific redox pathways is of particular importance.

To overcome the limitations and to better control the redox behavior of ZnO, various modification strategies have been explored, including doping with metal ions, forming complex nanostructures, or composites with other oxides ⁷⁻⁹. Currently, increasing attention is being focused on the development of hybrids of ZnO with carbon nanomaterials, including carbon dots (CDs) ^{10,11}. CDs are nanosized, quasi-spherical carbon particles, typically less than 10 nm in diameter ^{10,12}. They are characterized by broad, intense absorption in the UV and visible ranges, high solubility in polar solvents, and many surface functional groups ¹²⁻¹⁴. Their optical and electronic properties can be also adjusted through their structure, composition, and surface chemistry. Due to their low toxicity and biocompatibility, CDs are particularly promising as co-catalysts or modifiers for ZnO-based photocatalytic systems ^{15,16}. In ZnO-CDs hybrids, CDs extend the photoresponse of ZnO into the visible region and facilitate interfacial charge transfer, thereby reducing charge carrier recombination. Notably, their role can be limited not only to improving the overall efficiency of ZnO-based photocatalysts but may also influence the specific pathways of redox processes and increase the efficiency of reduction or oxidation reactions ^{12,13,16-18}. To assess the practical performance of these hybrid systems in the visible light range, the degradation of naproxen (NPX) was investigated as a model photocatalytic reaction. Naproxen, a widely monitored nonsteroidal anti-inflammatory drug, represents a class of persistent organic pollutants characterized by limited biodegradability in conventional wastewater treatment plants, making it a suitable material for assessing the enhanced visible light activity of the prepared photocatalysts ¹⁹⁻²¹.

The aim of this study was to determine whether the photocatalytic behavior of ZnO can be tuned toward reduction- or oxidation-driven processes by incorporating CDs through tailored surface modifications. Since the selectivity of such hybrid systems depends on the electronic coupling and charge transfer kinetics at the boundaries of both phases, achieving precise control over the hybrid architecture is important. For this purpose, various interfacial engineering strategies were deployed to immobilize CDs using distinct impregnation methods: simple impregnation, hydrothermal impregnation, APTES-based impregnation, and electrostatic adsorption. The obtained binary materials were compared in terms of their physicochemical properties, light absorption, charge-transfer behavior, and photocatalytic performance in selected reactions, including reduction (H_2O_2 production, $\text{O}_2^{\bullet-}$ generation) and oxidation ($\text{HO}^\bullet$ generation, naproxen degradation).

Although ZnO-CD photocatalysts have been widely studied, most reports focus on overall enhancements in photocatalytic activity, whereas the role of the modification route in directing the dominant redox pathway remains underexplored. This work aims not only to assess whether and how the use of CDs enhances ZnO activity but also to identify the optimal strategy for synthesizing the hybrid material for a specific reaction of interest.

2. Experimental

2.1. Materials and synthesis method

ZnO Synthesis: 5 g of zinc acetate was dissolved in 100 mL of distilled water by stirring at 60°C until complete dissolution. A 2 M NaOH solution was added dropwise to the solution until the pH reached 7-8. As a result, the precipitate of Zn(OH)₂ was formed. The suspension was left at 80°C for 2 hours, then the precipitate was centrifuged and washed three times with water and once with ethanol. To obtain ZnO, the precipitate was calcined at 450°C for 180 minutes.

CDs Synthesis: 26 mg of 3,4,9,10-perylene tetracarboxylic dianhydride was added to a mixture of 1 mL of triethylamine and 4 mL of N,N-dimethylformamide. The mixture was placed in a sealed Teflon-lined stainless-steel reactor and heated to 220°C for 48 hours. The resulting suspension was purified using a paper filter to remove any larger reaction residues. Nylon membrane syringe filters with 0.22 µm pore sizes were used to remove impurities.

Modified ZnO by APTES

100 mg of ZnO was suspended in 50 mL of ethanol and ultrasonicated for approximately 5-10 min. 0.5 mL of (3-Aminopropyl)triethoxysilane (APTES) was added and stirred for 2 h at 50°C, partially covered. The resulting suspension was centrifuged, and the precipitate was washed three times with ethanol and dried at 80° C overnight in air. This sample was labeled with the letter “A”.

Impregnation

IMP/ A_IMP: 100 mg of ZnO/ZnO_A together with 20 mg of CDs were suspended in 20 mL of distilled water. This suspension was placed on a shaker (180 rpm) for 3 hours. It was then centrifuged and dried at 80° C overnight in air.

Hydrothermal impregnation

IMP_H/ A_IMP_H: 100 mg of ZnO/ZnO_A was suspended in 20 mL of water, and 20 mg of CDs were added. The solution was placed in a sealed Teflon-lined stainless-steel reactor and heated to 140°C for 4 hours. The material was obtained by centrifugation from the solution.

Electrostatic Adsorption

ADS_E: 100 mg of ZnO was suspended in 50 mL of distilled water. The pH of the suspension was adjusted to 6.8. 20 mg of CDs were slowly added, and the mixture was stirred magnetically for 3 hours at 40°C. The precipitate was then washed with water and dried at 80° C overnight in air.

2.2.Equipment

The crystal structure of the materials was investigated using a PANalytical X'PERT PRO diffractometer using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). XRD measurements were performed at room temperature in the angular range $2\Theta = 10\text{--}80^\circ$ with a step size of 0.03° . Morphology analysis was performed using transmission electron microscopy (TEM) on a Philips CM20 Super Twin operating at 160 kV. Functional group identification was performed using infrared spectroscopy (IR) (Nicolet iSTM50, Thermo Fisher Scientific, Waltham, USA) in transmittance mode at $4000\text{--}400 \text{ cm}^{-1}$ range. The KBr pellets and samples were prepared for each IR spectrum. Absorption measurements were performed using a Varian Model 5E spectrophotometer (200–800 nm range, 0.1 nm spectral bandwidth). The specific surface area of the photocatalysts was measured by the Brunauer-Emmett-Teller (BET) method using a BSD-660M analyzer (Beishide Instrument, Beijing, China). All samples were degassed at 150 °C for 2 hours before N_2 adsorption-desorption measurements. The BET surface area was determined by a multipoint BET method. Emission characterization was performed on an FLS1000 spectrofluorometer from Edinburgh Instruments (Livingston, UK). The device was equipped with a 450 W xenon lamp as a continuous light source. Luminescence decay kinetics (lifetimes) were also measured on the FLS1000 using pulsed laser diodes at two excitation wavelengths of 375 and 450 nm.

2.3. Evaluation of the photocatalytic activity

Depending on the mechanisms of charge carrier generation and transport, the prepared binary photocatalysts may be more suitable for oxidation or reduction reactions. In this regard, the photocatalytic activity was evaluated for several redox reactions, including

H₂O₂ production, naproxen degradation, O₂^{•-} and HO[•] generation, and oxidation. These processes in slurry systems were performed in a 25 mL quartz reactor connected to a thermostat set to 20 °C. In the case of H₂O₂ production, a constant air flow of 10 l/h was introduced into the suspension during the reaction. A 300 W xenon lamp (model 6271H, Oriel, USA) with a water IR filter was used as a light source. To verify if the binary photocatalysts are visible-light-responsive, a cut-off filter above 420 nm was used. A detailed description of the system was presented in a previous article ²². In a typical reaction procedure, 25 mg of the catalyst (1 g/l) was dispersed under stirring in an aqueous NPX solution ([NPX]₀ = 15 mg/l), or, in the case of the H₂O₂ production, in a 10% (v/v) isopropanol/water mixture. Before irradiation, the photocatalyst suspension had been stirred for 30 min in the dark to establish the adsorption-desorption equilibrium. At preset time intervals, 1 mL samples of the suspension were collected and filtered through PET Chromafil® syringe filters with a pore size of 0.2 µm to remove photocatalyst particles from the water samples.

The NPX concentration in the filtrate was monitored using a high-performance liquid chromatography system (HPLC, Shimadzu LC-6A), combined with a photodiode array detector (SPD-M20A) and C18 column (Phenomenex Gemini 5 µm; 150x4.6 mm). During HPLC measurements, the mobile phase was composed of (v/v) 70% acetonitrile and 30% water with 0.1% formic acid at a flow rate of 0.35 mL/min. The signal originating from NPX had a retention time of 7.1 min and a λ_{max} of 230 nm. Quantitative analysis of NPX was performed utilizing the external calibration method. An HPLC-grade acetonitrile and formic acid solution was provided by Merck.

The concentration of generated H₂O₂ was measured using an iodometric method. For this procedure, 1 mL of the filtered liquid sample was mixed with 1 mL of a 0.2 M potassium phthalate solution and 1 cm³ of a 0.4 M potassium iodide solution, kept in the dark for 5 min, and then analyzed. The maximum absorbance attributed to H₂O₂ production was at λ_{max} = 350 nm. The UV-vis spectrophotometer (Thermo Scientific Evolution 220), equipped with quartz cuvettes with a 1 cm path length, was used for absorption measurements.

The photocatalytic generation of hydroxyl radicals (•OH) was investigated by studying the oxidation of coumarin to 7-hydroxycoumarin (7-OHC) ²³. The photocatalyst was suspended at 0.5 mM aqueous coumarin solution. The evolution of 7-OHC was monitored

by PL spectroscopy, with an external calibration curve for quantification. During the measurements, the excitation and emission wavelengths were 332 nm and 454 nm, respectively.

The photocatalytic production of superoxide radicals ($\cdot\text{O}_2^-$) was evaluated using a colorimetric method with 4-chloro-7-nitrobenzofurazan (NBD-Cl) as a chemical probe²⁴. Experiments were carried out with a 0.5 mM aqueous solution of NBD-Cl, and the relative amount of generated $\cdot\text{O}_2^-$ was determined by its characteristic absorbance at 470 nm. The concentration of $\cdot\text{O}_2^-$ was calculated using the known extinction coefficient of the product equal to $4000 \text{ M}^{-1} \cdot \text{cm}^{-1}$.

2.4.Data Analysis

2.4.1. Lattice parameters and unit cell analysis

The structural analysis of the synthesized ZnO-based hybrids was performed based on XRD patterns. The interplanar spacing (d_{hkl}) for the specific crystallographic planes was determined using Bragg's Law:

$$2d_{hkl}\sin\theta = n\lambda \quad (1)$$

where n is the order of reflection, λ is the X-ray wavelength ($1.5406 \text{ \AA}$ for Cu $K\alpha$), d_{hkl} is the interplanar spacing, and θ is the Bragg angle.

For the hexagonal wurtzite structure of ZnO, the relationship between the interplanar spacing d_{hkl} and the lattice parameters a and c are given by the following geometric formula:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (2)$$

To determine the lattice constants a and c , the diffraction peaks corresponding to the (100) and (002) planes were utilized. For the (100) plane ($h=1, k=0, l=0$) the formula simplifies for the direct calculation of the parameter a :

$$a = \frac{l}{(\sqrt{3}\sin\theta)} \quad (3)$$

Similarly, for the (002) plane ($h=0, k=0, l=2$) the lattice parameter c was calculated using simplified relation:

$$c = \frac{l}{\sin\theta} \quad (4)$$

The unit cell volume (V) for the hexagonal system was subsequently calculated using following equation:

$$V = \left(\frac{\sqrt{3}}{2}\right)a^2c \quad (5)$$

To evaluate the impact of CDs on the ZnO crystal lattice, the relative change in the unit cell volume (V) was calculated as a percentage difference compared to the pure ZnO reference:

$$\Delta V = \left(\frac{V_{sample} - V_{ZnO}}{V_{ZnO}}\right) \cdot 100\% \quad (6)$$

2.4.2. Determination of the optical bandgap energy

The energy gap (E_g) width was determined based on the Kubelka-Munk theory, which describes the diffuse reflection of light in particles that are comparable in size to or smaller than the wavelength of the incident light ^{25,26}. The functional relationship is described by the equation:

$$F(R_\infty) = \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (7)$$

where K and S are the absorption and scattering coefficients, respectively. Assuming a parabolic band model and the Tauc relation, E_g was determined by extrapolating the linear portion of the graph $[F(R_\infty)h\nu]^2$ versus photon energy ($h\nu$), assuming an exponent of $n = \frac{1}{2}$ appropriate for direct transitions.

3. Results and discussion

3.1. Structure and morphology

X-Ray diffraction (XRD)

The crystal structure of the obtained ZnO and its hybrids with CDs was analyzed by XRD (Fig. 1), comparing the diffraction patterns with the reference standard for hexagonal ZnO (ICSD#44505). This comparison showed full agreement of the positions of all recorded reflections with the standard data, confirming the production of a pure wurtzite phase without any admixtures of other crystalline phases ^{12,27-29}. The ZnO spectrum exhibits three dominant reflections at 2θ angles of 31.79° , 34.44° , and 36.27° , corresponding to the (100), (002), and (101) lattice planes, respectively. The remaining, lower-intensity reflections, visible at angles of 47.56° (102), 56.62° (110), 62.88° (103), and in the $66-70^\circ$ 2θ region, are also consistent with the reference positions.

The absence of bands characteristic of CDs results from their small size and the low mass fraction of the carbon phase relative to the inorganic matrix. The high agreement with the reference across all samples confirms that the support maintains its structural integrity under various processing conditions, including hydrothermal interactions and electrostatic modifications.

Analysis of the diffraction patterns of the obtained hybrid materials revealed a systematic shift of the peaks toward higher 2θ degrees compared to pure ZnO. In accordance with Bragg's law, the shift toward higher angles indicates contraction of the crystal lattice and a reduction in the interplanar d-spacing in the ZnO structure. The magnitude of the observed shifts clearly depends on the surface modification method used. The largest angular shift was observed for the sample obtained by the hydrothermal method (IMP_H), while the smallest was observed for the sample obtained by the hydrothermal method and using the APTES (A_IMP_H). These differences suggest the generation of variable compressive stresses into the ZnO crystalline lattice, resulting from the different nature of interactions at the ZnO-CDs interfaces. At the same time, an increase in the full width at half height (FWHM) of the peaks was observed in all modified samples. This broadening indicates a decrease in the average crystallite size as well as increase in structural disorder and lattice microstrain, which directly correlates with the above-mentioned stresses induced in the network.

The structural parameters of the synthesized samples were further analyzed based on XRD data to assess the effect of CDs on the wurtzite ZnO lattice. As summarized in Table 1, a change in the lattice parameters a and c and a subsequent reduction in the unit cell volume (V). The largest lattice shrinkage was observed in samples IMP_H and ADS_E, with unit cell volume decreases of 1.36% and 0.98%, respectively. Such changes in lattice constants provide direct evidence for lattice deformation and strong interfacial interactions between ZnO and CDs. Interestingly, sample A_IMP_H was characterized by the smallest change in unit cell volume (-0.03%) compared to pure ZnO. The observed crystal lattice deformation and increase in FWHM, particularly for the ADS_E sample, correlate with a decrease in crystallite size and an increase in surface defect density^{12,30}.

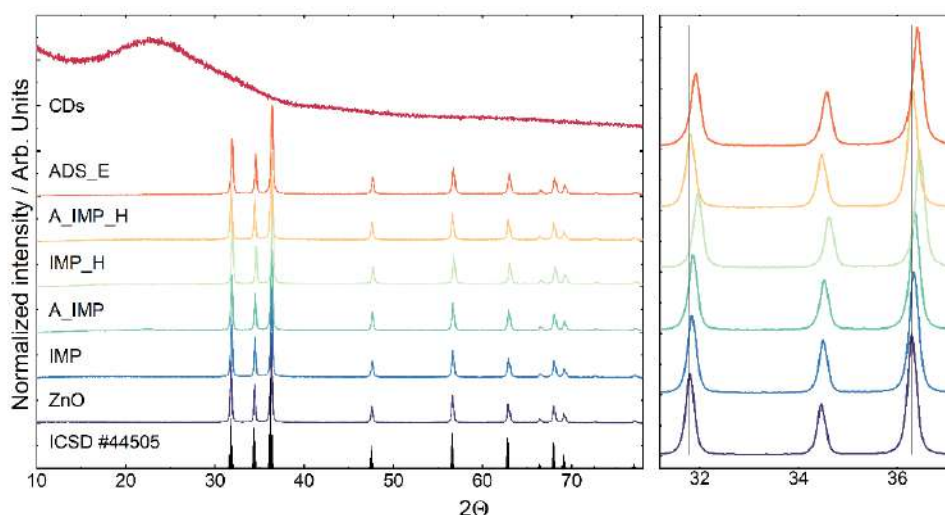


Figure 1. XRD diffractogram of unmodified ZnO, hybrid materials, and pure CDs.

Table 1. Lattice parameters and unit cell volume for the CDs@ZnO hybrid materials.

Próbka	a [Å]	c [Å]	c/a	V [Å ³]	ΔV [%]
ZnO	3.2457	5.2011	1.6024	47.4509	
IMP	3.2417	5.1952	1.6026	47.2816	-0.3567
A_IMP	3.2408	5.1923	1.6022	47.2262	-0.4736
IMP_H	3.2309	5.1778	1.6026	46.8073	-1.3563
A_IMP_H	3.2457	5.1996	1.6020	47.4375	-0.0281
ADS_E	3.2348	5.1850	1.6029	46.9874	-0.9767

TEM

TEM image analysis revealed the crystalline structure of all materials obtained (Fig. 2). The dominant feature is extended agglomerates with dimensions of 50-400 nm, formed by sintering of primary grains during calcination. This structure provides a framework for the deposited carbon phases. The initial ZnO exhibits a morphology typical of oxides obtained by the precipitation-calcination method. Crystallites with smooth surfaces and sharp edges are visible, joined into compact aggregates. The material is homogeneous, and no amorphous phases or organic impurities are observed in the images. Small pores are visible on the crystallite surfaces.

The IMP sample shows the smallest changes compared to the reference. The agglomerates retain their original, smooth structure. The lack of contrast changes at the crystallite edges

suggests that the CDs are dispersed and weakly bound to the substrate, confirming the low deposition efficiency under room conditions without supporting agents.

In conventional impregnation, APTES modification introduces a thin organic layer onto the ZnO surface, consisting of a cross-linked polysiloxane (Si-O-Si) network bearing aminopropyl functional groups. A slight blurring of the agglomerate contours is visible, indicating the presence of a polymeric silane layer, which acts as a molecular "glue" for the CDs.

In the case of hydrothermal impregnation, an additional amorphous layer can be observed, demonstrating that the hydrothermal conditions themselves force stronger adhesion of the carbon phase. The dots not only deposit on the surface but can also form a thin hybrid film, accompanied by a more pronounced disruption of the pristine ZnO agglomerates.

Combining hydrothermal impregnation with APTES modification creates a distinct shell. The combination of a chemical linker and pressure treatment led to the formation of a distinct, continuous hybrid layer several nanometers thick that tightly enveloped the crystalline ZnO core and effectively protected the oxide from disintegration of agglomerates. This layer is densely saturated with CDs, making this system the most exemplary core-shell structure in the entire series ^{12,27,28}.

ADS_E stands out from the others with its unique edge morphology. Characteristic "finger-like" crystalline protrusions are observed on the surface of the ZnO agglomerates. These elongated nanostructures, absent in other samples, suggest that the adsorption process conducted at a specific pH (the electrostatic point of ZnO) may have induced local surface reorganization or selective growth on active crystallographic centers. These "finger-like" forms increase the contact area between ZnO and CDs, which, combined with their high degree of dispersion, makes this method effective from a physicochemical perspective ^{12,28,30}.

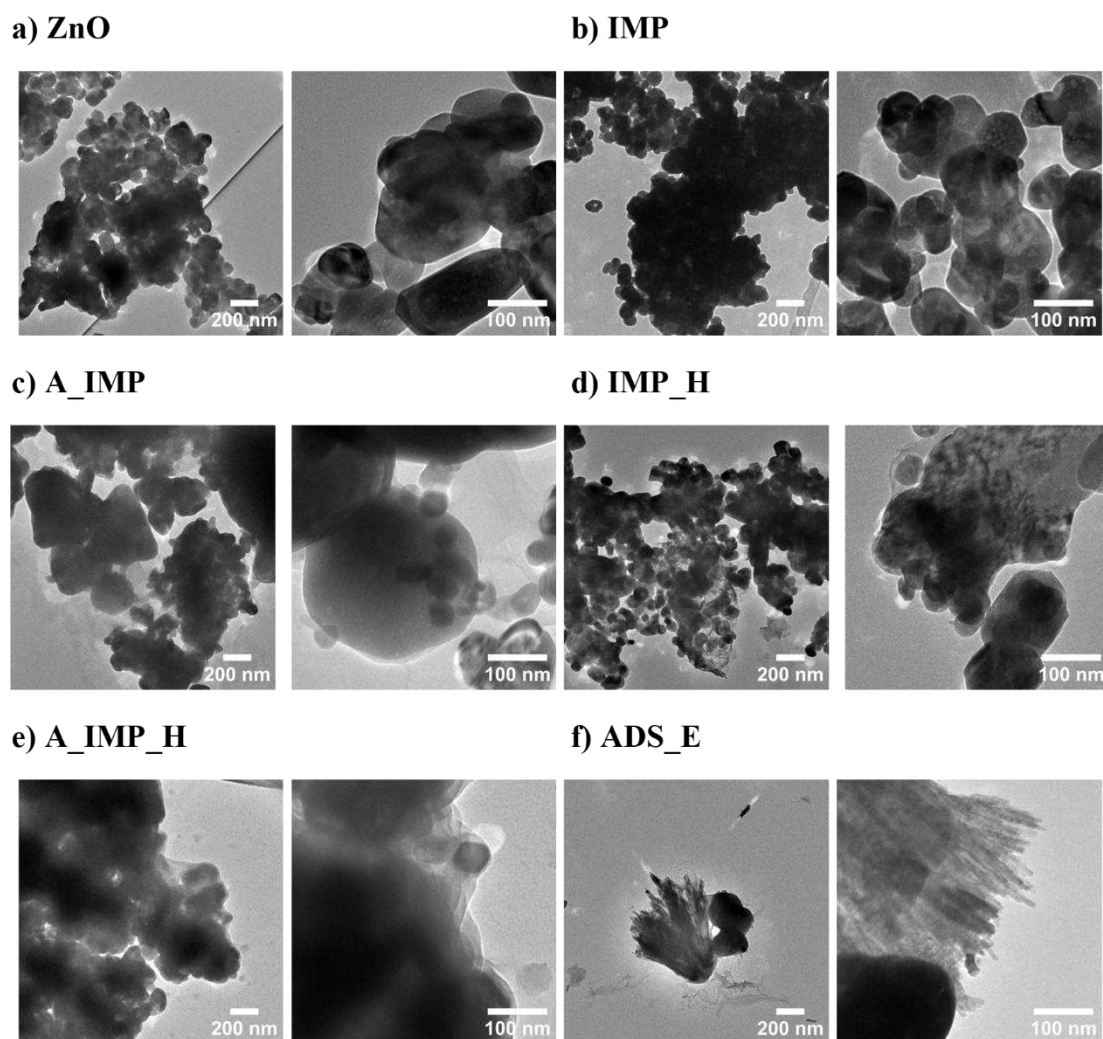


Figure 2. TEM image of a) pure ZnO, b) IMP, c) A_IMP, d) IMP_H, e) A_IMP_H, and f) ADS_E for different magnifications.

The Brunauer-Emmett-Teller (BET)

To determine the effect of the applied surface modification strategies on the structural and textural properties of pure ZnO and CDs@ZnO hybrids, nitrogen adsorption-desorption measurements were performed. Based on the obtained isotherms (Fig. 3), the specific surface area (S_{BET}) and the total pore volume (V_{total}) were determined using the Brunauer-Emmett-Teller method. Detailed textural parameters of the tested materials are summarized in Table 2.

Analysis of ZnO showed a relatively low S_{BET} and V_{total} , which is characteristic for materials obtained by the precipitation method followed by calcination. The introduction of CDs *via* classical impregnation led to decreases in S_{BET} and pore volume. This effect can be attributed to the partial blocking of the ZnO's existing pores by loosely bound and dispersed CDs. This observation correlates with TEM observations indicating weak

binding of the carbon phase. A similar trend was noted for the A_IMP sample, where the presence of APTES layer limits the accessibility of the porous ZnO surface.

Different changes were observed in the synthesis conducted under hydrothermal conditions. The IMP_H sample showed a more than twofold increase in S_{BET} , reaching the highest value in this series of measurements, accompanied by an increase in V_{total} . This change in texture results from increased pressure and temperature in the autoclave, which effectively disrupts the large, compact ZnO aggregates formed during calcination. This process likely occurs through partial, superficial dissolution of the sintering points that hold the grains together, thereby disintegrating secondary agglomerates. As a result, a new, previously inaccessible specific surface area is exposed, and intergranular pores are unblocked. The strong impact of the pressure prevailing in the autoclave on the released single crystallites is also confirmed by XRD analysis, which, in this case, showed the highest shrinkage of the unit cell.

In the case of sample A_IMP_H, where hydrothermal treatment was preceded by silane modification, S_{BET} and V_{total} remained almost identical to those of pure ZnO. The presence of an APTES layer on the ZnO surface before the hydrothermal stage alters the material's susceptibility to disintegration. Through strong Si-O-Zn bonds, APTES mechanically binds the ZnO grains within the existing aggregates and forms a protective organic shell around them. As a result, the aggregates are thus protected, exhibiting higher mechanical and chemical resistance to hydrothermal conditions and preventing them from breaking down under autoclave pressure. This corresponds with the lack of changes in the unit cell volume for this sample. The lack of a decrease in textural parameters for sample A_IMP_H suggests that elevated pressure promotes simultaneous spatial reorganization of the hybrid layer, resulting in slight loosening and the formation of local micropores within the silica-organic structure.

The sample obtained via electrostatic adsorption exhibited increases in S_{BET} and V_{total} . This also correlates well with the results of XRD and TEM. Controlling the pH of the environment induced local surface reorganization and the selective growth of characteristic, elongated, finger-like crystalline protrusions. The formation of these nanostructures increases the contact surface area, thereby increasing the dispersion of CDs and improving the textural parameters of the final photocatalyst.

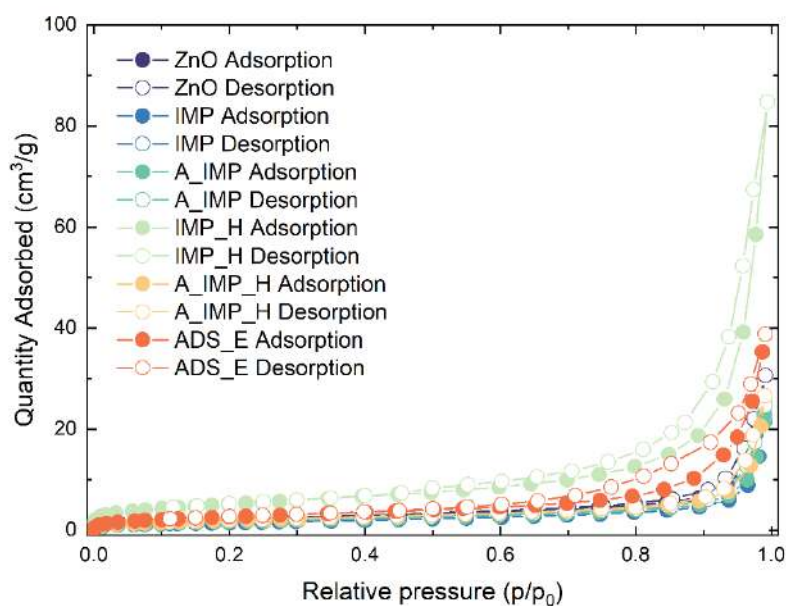


Figure 3. N₂ adsorption-desorption isotherms of pure ZnO and CDs@ZnO hybrids materials.

Table 2. Textural properties of ZnO and CDs@ZnO.

Sample	S _{BET} [m ² /g]	V _{total} [cm ³ /g]
ZnO	7.70	0.05
IMP	5.40	0.03
A_IMP	6.37	0.04
IMP_H	18.58	0.12
A_IMP_H	7.34	0.04
ADS_E	10.00	0.06

IR

Infrared spectroscopic analysis allowed the identification of the functional groups present on the surface of the obtained materials and assessed the effectiveness of the impregnation processes (Fig. 4). The spectrum of pure ZnO serves as a reference point, revealing the high hydrophilicity and adsorption activity of its surface¹². The dominant signal in the high wavenumber region is a broad, asymmetric band in the 3200-3600 cm⁻¹ range, arising from adsorbed water and the stretching vibrations of surface hydroxyl groups bound by hydrogen bonds²⁷. Importantly, this spectrum also includes distinct bands in the 1250-1750 cm⁻¹ region, which can be attributed to the symmetric and asymmetric

stretching vibrations of the carboxyl groups (-COO^-)¹⁵. Their presence suggests acetate precursors, leading to the formation of surface carbonate species and confirming the presence of basic centers on the oxide surface.

The spectrum of pure CDs displays a complex band profile, indicating their rich chemical structure. A broad band in the $3100\text{-}3600\text{ cm}^{-1}$ region corresponds to the stretching vibrations of the hydroxyl (-OH) and amine (-NH) groups, which results from the presence of surface groups^{27,31}. The presence of carboxyl groups (C=O) originating from imide rings or carboxyl groups and the aromatic perylene skeleton is confirmed by intense peaks in the $1700\text{-}1400\text{ cm}^{-1}$ range.

The hybrid formation process leads to a synergistic superposition of the signals of both components, but with distinct modifications indicating the stability of the bond (Table 3)³². The appearance of bands at 2935 and 2860 cm^{-1} was observed in the spectra of the hydrothermally modified materials. These bands correspond to asymmetric and symmetric stretching vibrations of the C-H bonds. Concurrently, the signal enhancement in the region of 1565 cm^{-1} , attributed to the bending vibrations of -NH_2 groups, was also predominantly noted for the IMP_H and A_IMP_H samples. This confirms the presence of amine functionalities, which likely originate from the CDs structure and are more effectively stabilized or incorporated during the hydrothermal treatment.

Modified spectral features appear in hybrid materials but are absent or unresolved in both pure ZnO and CDs. Rather than the formation of entirely new chemical bonds, these changes indicate that the hidden or overlapped vibrational modes of CDs effectively emerge and become unmasked upon interaction with the matrix. A new band appears at approximately 1360 cm^{-1} for hydrothermally treated and silanized hybrids. This peak is attributed to the rigid C-N stretching vibrations of the transformed imide/amide structures, demonstrating that the chemical environment of the dots becomes structurally rigid and locked onto the ZnO surface. At the same time, a change is observed for the band located at approximately 1300 cm^{-1} in the spectrum of free CDs, which is assigned to the C-O/C-O-C stretching modes of oxygen-containing groups. In all obtained hybrid materials, this band disappears, while the adjacent component originating from CDs near 1360 cm^{-1} becomes sharper. The disappearance of the 1300 cm^{-1} band provides direct chemical evidence that the oxygen-containing functional groups on the CDs surface are consumed during the immobilization process, acting as the main anchoring centers that connect the carbon phase directly to the zinc atoms of the ZnO matrix. Furthermore, the

new peaks at 1570 and 1590 cm^{-1} reflect the characteristic spectral components of CDs, which are effectively resolved and unmasked in the hybrids, whereas they overlap as a single, broader band in the ATR spectrum of CDs. The appearance of the peak at 1570 cm^{-1} corresponds to the ordered asymmetric vibrations of the deprotonated carboxyl groups ($-\text{COO}^-$) bound to Zn^{2+} , while the peak at 1590 cm^{-1} represents the structural stabilization of the skeletal vibrations of the aromatic $\text{C}=\text{C}$ core in the perylene lattice, resulting from its planar, rigid arrangement.

The ADS_E material stands out among the other hybrids, exhibiting a broader spectrum induced by pH-controlled electrostatic adsorption. In this sample, a new band at 1500 cm^{-1} appears, which is absent in the other materials. This peak results from the symmetric stretching vibrations of the carboxylate groups, coupled to the zinc centers under the influence of precise electrostatic forces. Additionally, the broad carbonyl band, typically located around 1630 cm^{-1} , changes in the ADS_E spectrum compared to the other samples becoming sharper and more intense. This indicates that the strong Coulomb forces between the positive surface potential of ZnO and the negatively charged outer layer of dots effectively disrupt the hydrogen bonding networks of CDs, forcing a uniform, dense packing and distinct spatial orientation of the carbon phase on the oxide surface. Against this background, the spectrum of the IMP sample exhibits the lowest intensity of bands characteristic of the carbon phase, particularly in the region of the stretching vibrations of the $\text{C}=\text{O}$ and $\text{C}-\text{H}$ bonds. This suggests that under room conditions, without additional energetic support or directed electrostatic interactions, CDs deposition on the ZnO surface occurs primarily *via* weak physisorption. Despite the lower dot packing density, key signals from the aromatic carbon skeleton in the 1400-1600 cm^{-1} range are still observable in this spectrum, confirming that even simple impregnation allows for the permanent binding of some CDs to the active ZnO surface centers.

Comparative analysis also reveals subtle shifts toward lower energies of the $\text{C}=\text{O}$ bands in the hybrids relative to the free CDs. This phenomenon provides direct evidence for the association of ZnO and CDs ¹². Additionally, the disappearance or broadening of the bands in the 1100 cm^{-1} region ($\text{C}-\text{O}$ stretching) suggests that the oxygen functional groups of the dots are involved in forming stable chemical bonds with zinc atoms on the support surface ³³. All these changes suggest that the obtained materials are not simple physical mixtures, but advanced hybrid systems ³⁴.

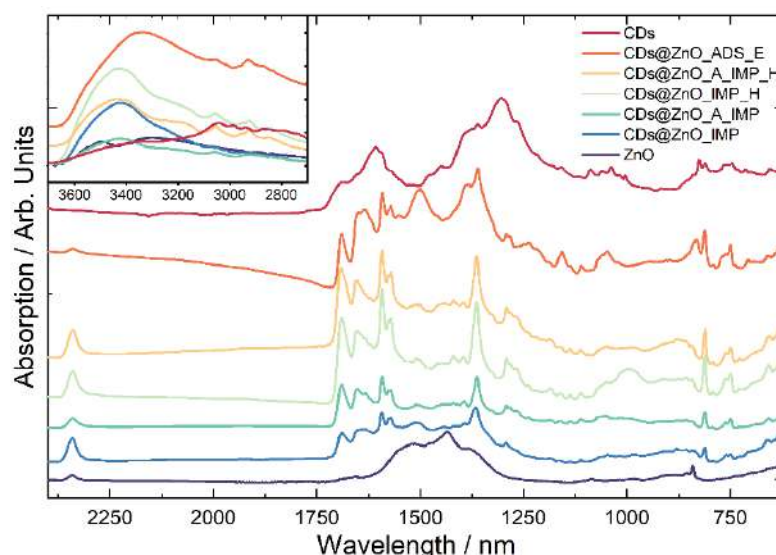


Figure 4. IR spectra of pure ZnO, CDs@ZnO hybrid materials, and CDs.

Table 3. Unique IR bands related to reference samples.

Sample	Unique bands (cm ⁻¹)
IMP	1580, 1395
A_IMP	2925, 2855, 1565
IMP_H	2935, 2860, 1690, 1570, 1360
A_IMP_H	2930, 2860, 1690, 1570, 1360
ADS_E	2930, 2860, 1630, 1600, 1550, 1500, 1360, 1020

3.2.Spectroscopic properties of CDs@ZnO hybrid materials

Absorption

Analysis of optical properties in the UV-Vis range allowed to assess changes in the absorption range and the activation ability of the hybrid materials (Fig.5). The spectrum of pure ZnO is characterized by a sharp increase in absorption below 380 nm, resulting from electronic transitions from the valence band to the conduction band, and low absorption in the visible range. The introduction of CDs modified the absorption spectrum, introducing an additional broad absorption band in the visible range (400-600 nm). The intensity of this range depends strictly on the impregnation method used, reaching the highest values for samples obtained by electrostatic adsorption and the lowest for samples in which ZnO was modified with APTES. This absorption is possible

due to the presence of functional groups on the CD surfaces, such as carbonyl and amine groups, which introduce additional energy levels (π - π^* and n - π^* transitions). Detailed analysis of the absorption edges revealed subtle changes in the materials' electronic structure (Table 4). The determined optical E_g values for all tested materials are within a narrow range of 3.18-3.21 eV. This suggests that the introduction of CDs and APTES surface modification does not alter the band structure of ZnO. The lack of shifts in E_g values also confirms that the synthesis processes (including hydrothermal treatment) do not induce profound structural changes in ZnO^{18,27}.

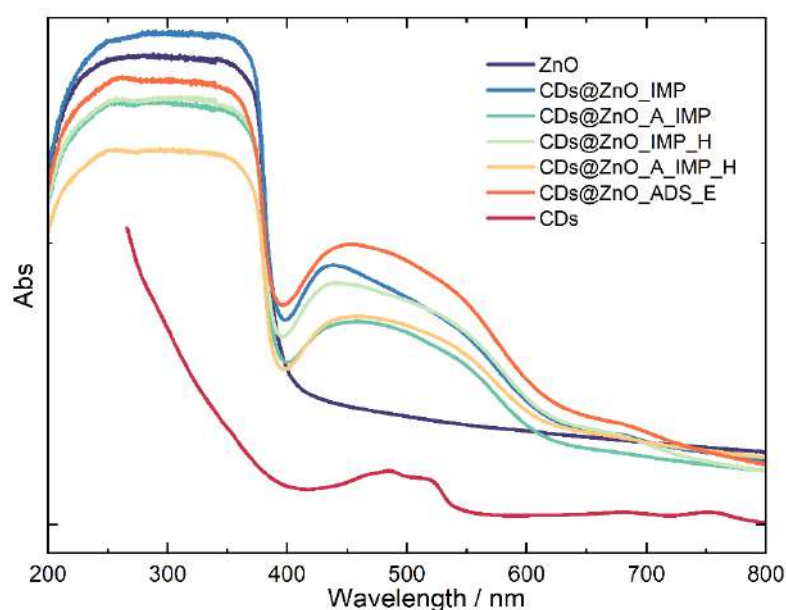


Figure 5. Absorption spectra for pure ZnO, CDs@ZnO hybrid materials and pure CDs.

Table 4. Band gap values determined for unmodified ZnO and obtained CDs@ZnO hybrid materials based on UV-Vis absorption spectra.

Sample	Bandgap [eV]
ZnO	3.18
IMP	3.20
A_IMP	3.21
IMP_H	3.21
A_IMP_H	3.19
ADS_E	3.19

Excitation

Analysis of the optical properties of hybrid systems, conducted using excitation measurements at an emission wavelength of 600 nm, provides key information on the interactions between the components of the hybrid materials and the efficiency of energy transfer (Fig. 6). In the ultraviolet region, the spectra of most materials exhibit a characteristic structure resulting from the overlap of two excitation bands. The first high-energy band peaks in the 357-361 nm range and is characterized by a larger FWHM (Table 5). However, due to the modification, it gradually narrows, reaching a minimum of 37.71 nm for the ADS_E sample. The second, low-energy band is located near the absorption edge of ZnO, with a maximum around 376-378 nm. This component is characterized by a lower FWHM, indicating its direct relationship with the band transitions of the oxide matrix. Mathematical analysis of the spectral fitting allowed for the determination of the A-factor, defined as the relative contribution of the first transition to the total excitation band ($\frac{A_1}{A_1+A_2}$) (Table 5.). For the ZnO, IMP and IMP_H samples, this factor remains at a stable level. In the case of the A_IMP_H sample, a slight increase in the contribution of the high-energy transition is observed. In the ADS_E sample, the UV spectrum is dominated by a single band with a maximum at 359 nm. The absence of a clearly defined second edge band in this material suggests that the ADS_E modification process led to a restructuring of energy states near the band gap or to the dominance of excitation channels associated with the introduced surface centers. This observation correlates with the observed morphological changes and the strongest dot packing on the surface.

The presence of visible bands is directly related to the presence of CDs on the semiconductor surface. The intensity of this band varies depending on the impregnation strategy used, suggesting a different degree of surface functionalization^{13,30}. The highest excitation efficiency in the visible range was observed for the A_IMP sample, indicating that using APTES without additional hydrothermal treatment preserves the optical characteristics of the CDs in the hybrid system. Samples subjected to the hydrothermal process (IMP_H and A_IMP_H) exhibit moderate signal intensity, which may be due to partial entrapment of CDs within the ZnO structure or to changes in their surface chemistry under high pressure conditions.

The key differences between the materials studied are evident in the ratio of excitation efficiency in the UV range to activity in the visible range (400-500 nm). For pure ZnO

and the IMP sample, this ratio is high, indicating that high energy radiation is the dominant source of luminescence. The introduction of modifications to the A_IMP samples changes the profile, with the broad band in the visible range becoming dominant. This indicates the creation of new, efficient excitation channels in the lower energy region. Hybrid samples, such as A_IMP_H and IMP_H, exhibit an intermediate character – they retain the optical properties of ZnO in the UV while demonstrating distinct activity in the visible.

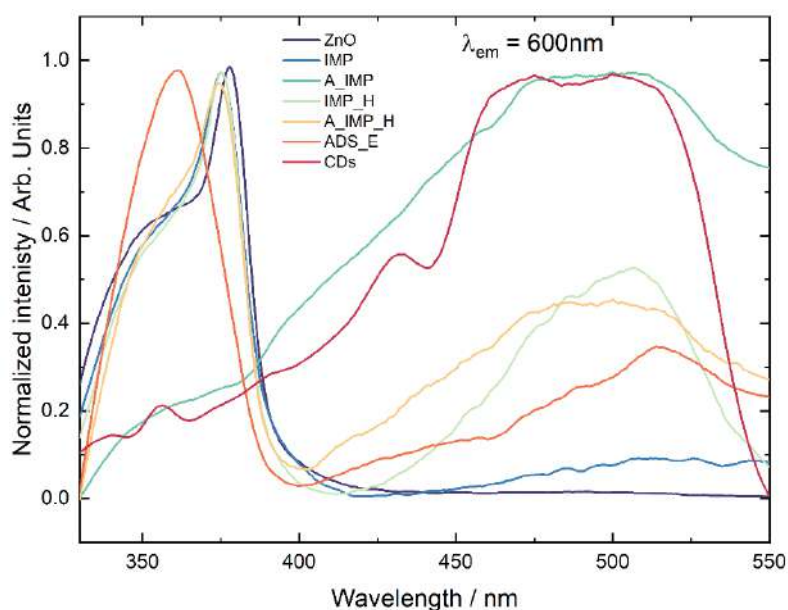


Figure 6. Normalized excitation spectra of unmodified ZnO, CDs and CDs@ZnO hybrid materials recorded for the emission wavelength of 600 nm.

Table 5. Summary of the maxima positions and FWHM of the excitation band components in the UV region for a CDs@ZnO hybrid materials.

		ZnO	IMP	IMP_H	A_IMP_H	ADS_E
1 st	λ_{max} [nm]	357.36	359.03	358.48	360.54	359.34
	FWHM [cm ⁻¹]	3628.12	3512.76	3285.94	3337.85	2916.75
2 nd	λ_{max} [nm]	378.19	376.00	376.11	376.12	
	FWHM [cm ⁻¹]	891.81	983.52	969.84	928.01	
A - factor		0.815055	0.808969	0.789135	0.852189	

Emission

The emission properties of the resulting materials were characterized using two excitation wavelengths: 360 and 510 nm. Excitation at 360 nm corresponds directly to the fundamental absorption edge of the ZnO, ensuring the generation of electron-hole pairs. Excitation at 510 nm was chosen to selectively affect the carbon phase and interfacial states without background interference from the semiconductor. These values were selected based on the absorption and excitation spectra. The spectra obtained under 360 nm excitation reveal a complex band structure resulting from the synergistic combination of ZnO and CDs (Fig. 7a). The spectrum of pure ZnO exhibits a band in the 380-390 nm range and a dominant broad band in the visible range, with a maximum at approximately 650 nm, attributed to radiative transitions associated with structural defects such as oxygen vacancies.

The spectrum of pure CDs recorded under 360 nm excitation exhibits a distinct, complex emission profile. This directly indicates the coexistence of multiple emission centers in the CDs structure, a phenomenon consistent with the multicenter emission model ³¹. Detailed analysis of the spectral components performed using band deconvolution (Table 6), revealed five distinct components. Bands located in the 450-470 nm range are attributed to the internal core states of the CDs, resulting from π - π^* electronic transitions within conjugated sp^2 domains. Bands in the 540-580 nm range, on the other hand, represent radiative recombination through surface trap states (STS), associated with nitrogen- and oxygen-containing functional groups. Stabilization of these traps promotes efficient charge transfer from the core to the surface, resulting in emissions above 600 nm. Deconvolution analysis confirms that the surface modification strategy affects the electronic structure of the hybrid materials. A band in the 380–390 nm range was identified for all composites. It is worth noting that the ADS_E sample exhibits a shift of this maximum toward longer wavelengths and a broadening of the signal, suggesting a change in excitonic states due to the dense packing of CDs on the semiconductor surface ³⁵. In the visible region, the introduction of CDs caused a red-shift of the main band and its narrowing. The appearance of a new high-intensity component with a maximum around 715 nm indicates the passivation of deep oxygen traps in ZnO and the formation of new recombination channels at the interface ¹³.

Emission intensity analysis (Fig. 7c) showed that using simple impregnation and the hydrothermal method (IMP and IMP_H) increased luminescence intensity in the visible range relative to pure ZnO. This indicates that in these systems, CDs act as the main

emission centers, not creating efficient paths for non-radiative energy transfer. The ADS_E sample exhibited a moderate increase in intensity, whereas the materials in which APTES were used showed a decrease in luminescence intensity in the visible range compared to pure ZnO. This is particularly evident for A_IMP_H. This pronounced quenching of defect emission, accompanied by a simultaneous enhancement of edge emission in the UV, is interpreted as evidence of strong chemical bonding between the components and effective charge transfer.

Excitation at 510 nm (Fig. 7b, d) activates the carbon phase and interfacial states. The absence of a signal for pure ZnO under these conditions confirms that the observed response of the hybrid materials is a direct result of the modification. Emission analysis of pure CDs reveals three distinct bands. Comparison of these results with emission from higher-energy excitation shows that the band positions remain nearly constant, confirming the high-energy stability of the STS under both excitations. Deconvolution of these spectra revealed a shift in the hybrid materials' peaks toward lower energies relative to pure CDs. The highest luminescence efficiency in this range was observed for sample A_IMP, suggesting that molecular bonding without hydrothermal treatment best preserves the optical activity of CDs. In contrast, for samples A_IMP_H and ADS_E, the dominance of emission in the red range at lower intensities indicates the formation of deep trap states or strong π - π interactions between the dots^{31,36}.

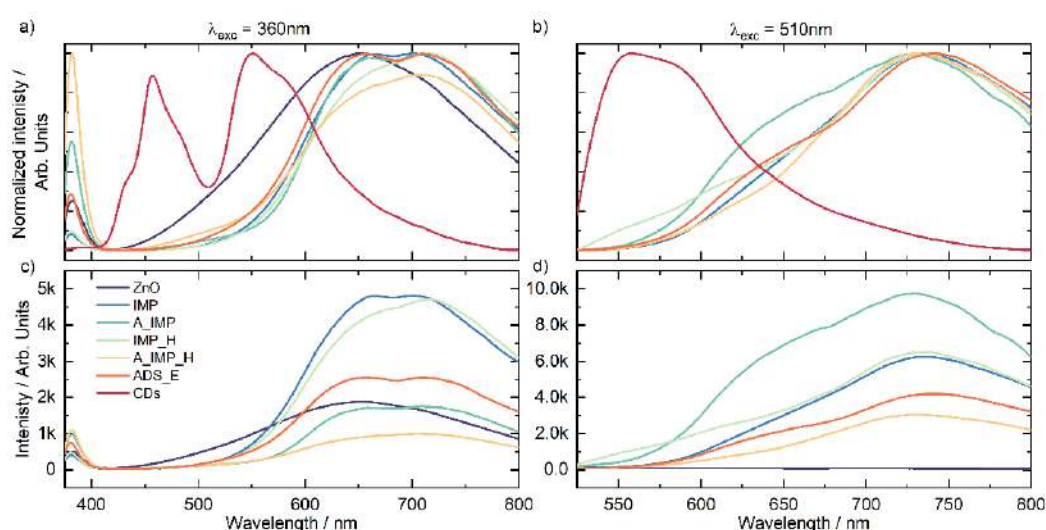


Figure 7. Normalized (a,b) and non-normalized (c,d) emission spectra of pure ZnO, CDs@ZnO hybrid materials, and unmodified CDs, under 360 (a,c) and 510 (b,d) nm excitation.

Table 6. Summary of the maxima positions and FWHM of the emission band components for CDs@ZnO hybrid materials.

		ZnO	IMP	A_IMP	IMP_H	A_IMP_H	ADS_E	CDs
$\lambda_{\text{exc}} = 360 \text{ nm}$								
1 st	λ_{max} [nm]	382.5	381.6	381.9	381.4	382.1	388.6	455.7
2 nd	λ_{max} [nm]	648.3	635.3	631.1	630.1	629.2	627.4	463.2
3 rd	λ_{max} [nm]		720.0	710.5	721.8	716.1	710.7	544.2
4 th	λ_{max} [nm]							571.7
5 th	λ_{max} [nm]							618.6
$\lambda_{\text{exc}} = 510 \text{ nm}$								
1 st	λ_{max} [nm]		632.4	621.8	600.8	717.9	638.7	548.5
2 nd	λ_{max} [nm]		741.1	655.9	741.5	747.8	746.2	580.0
3 rd	λ_{max} [nm]			730.3				621.5

A comprehensive electron migration mechanism was proposed for both excitation wavelengths (360 nm and 510 nm), as shown in Figure 8. The formation of a hybrid architecture activates efficient, non-radiative relaxation channels that direct photogenerated carriers toward lower-energy states, thereby enabling alternative light paths and simultaneous emission from different defect levels. During excitation with 360 nm UV light (Figure 8a), electrons in ZnO occupy a level close to the band gap of approximately 3.24 eV. This level is present in all samples, demonstrating that CDs do not modify the energy structure of ZnO. In pure ZnO, electrons transition from this state to the defect level of 1.91 eV. However, in hybrid materials, this level shifts upward (to 1.95–1.97 eV) and is co-occupied by electrons from ZnO and, via interfacial charge transfer (ICT), from the CDs. The first visible radiative emission occurs from this elevated level. Simultaneously, some electrons relax non-radiatively to a deeper energy state, thereby activating an entirely new interfacial level at approximately 1.72 eV. As a result, the hybrid material generates a second, new emission in the deep red region, which was absent in the starting components themselves.

During excitation with visible light at a wavelength of 510 nm (Figure 8b), the photoexcitation processes are restricted exclusively to the CDs. Electrons from the CDs

relax non-radiatively to a trapping level at 1.94–2.06 eV, from which they emit. As with UV excitation, part of the charge cascades further into the interfacial level (shifted to 1.65–1.69 eV due to the lower excitation energy), thereby inducing a second emission. The exception is the optimized sample A_IMP_H, in which the higher level (1.94–2.06 eV) is quenched. This forces the electron to relax directly to the lowest interfacial level at 1.66 eV.

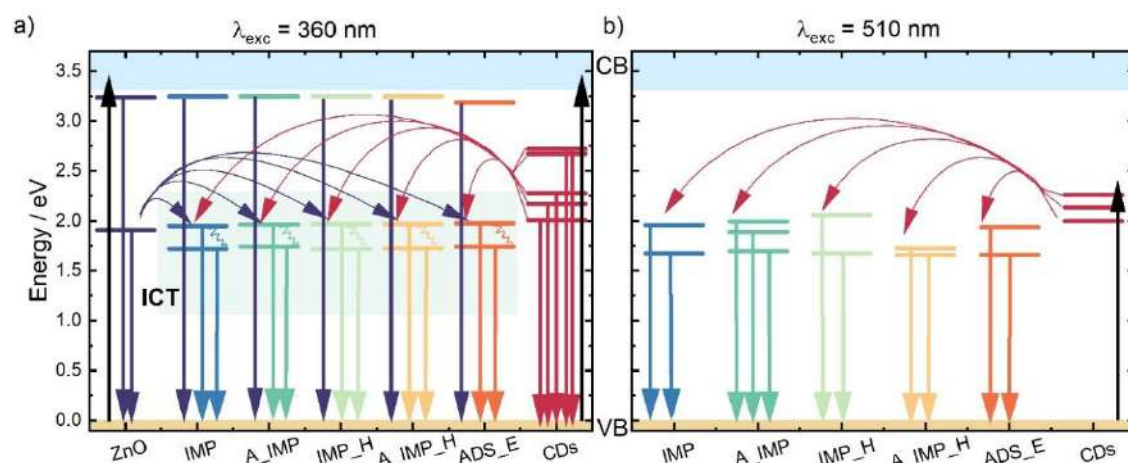


Figure 8. Mechanism of energy transfer in pure ZnO and CDs@ZnO hybrid materials. The highlighted CB and VB bands are determined by the ZnO band gap.

Luminescence kinetics

Measurements of the lifetimes of excited states allow for a precise determination of the effect of surface tailoring strategies on charge carrier kinetics in hybrid systems. The summarized data (Table 7) show a distinct difference in relaxation dynamics depending on the excitation and emission configurations, which directly reflects changes in the electronic structure at the CDs@ZnO interface. For measurements conducted at 375 nm excitation and 440 nm emission, most hybrid materials exhibit a slightly longer lifetime compared to pure ZnO, suggesting passivation of surface trap states by CDs¹⁵. Only the A_IMP_H sample showed a shorter lifetime, indicating the opening of additional, nonradiative relaxation channels.

The analysis of the deeper defect emission in ZnO ($\lambda_{\text{exc}} = 375$ nm, $\lambda_{\text{em}} = 600$ nm) reveals a distinct effect of impregnation strategies on charge transfer processes. For the A_IMP and IMP_H materials, lifetimes were reduced relative to pure ZnO, suggesting efficient electron transfer from ZnO defects to the carbon phase. Samples A_IMP_H and ADS_E

exhibit different dynamics, with longer decay times. This effect results from the structural reorganization of the ZnO surface during hydrothermal treatment or pH-controlled electrostatic packing. These specific assembly routes induce the formation of stable, long-lived interfacial trap states that effectively capture photogenerated carriers and delay their radiative recombination.

Analysis conducted under visible light excitation ($\lambda_{\text{exc}} = 450 \text{ nm}$, $\lambda_{\text{em}} = 650 \text{ nm}$) enabled assessment of the stability and dynamics of the carbon phase in the composite. An interesting observation is that samples ADS_E and A_IMP_H exhibit longer lifetimes among all synthesized hybrids, remaining closest to those of pure CDs. This prolonged relaxation time suggests that in these materials, CDs form stable configurations with the oxide, delaying non-radiative recombination channels. This indicates a strong interaction between the components or a specific organization of the CDs layer, which promotes stable charge separation^{37,38}. In contrast, the remaining samples exhibited shorter lifetimes due to more intense dynamic quenching. All samples also exhibited shorter lifetimes relative to pure CDs, indicating their binding to the ZnO matrix.

Table 7. Luminescence lifetime of pure ZnO and CDs@ZnO hybrid materials.

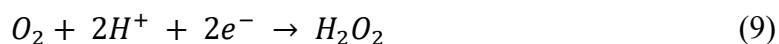
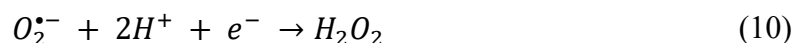
	$\lambda_{\text{exc}} = 375 \text{ nm}$ $\lambda_{\text{em}} = 440 \text{ nm}$	$\lambda_{\text{exc}} = 375 \text{ nm}$ $\lambda_{\text{em}} = 600 \text{ nm}$	$\lambda_{\text{exc}} = 450 \text{ nm}$ $\lambda_{\text{em}} = 650 \text{ nm}$
ZnO	1.41 ns	1.77 ns	4.13 ns
IMP	1.55 ns	1.71 ns	3.73 ns
A_IMP	1.75 ns	1.45 ns	3.53 ns
IMP_H	1.59 ns	1.55 ns	2.84 ns
A_IMP_H	1.37 ns	3.24 ns	4.81 ns
ADS_E	1.61 ns	2.5 ns	4.87 ns
CDs	3.34 ns	15.61 ns	6.00 ns

Photocatalytic activity

Generation of reactive oxygen species

The photocatalytic activity of CDs@ZnO samples was evaluated toward ROS generation under UV-Vis light, specifically $\bullet\text{OH}$ generation as an example of an oxidation reaction

(Eq. 8) and oxygen reduction to H₂O₂ (Eq. 9 and 10) (two-electron) or O₂^{•-} (single-electron) (Eq. 11), according to the equations below:



The efficiency of photocatalytic H₂O₂ generation under Xe lamp irradiation (UV-Vis) was dependent on the impregnation method of the hybrid materials (Fig. 9a). The IMP_H sample demonstrated the highest H₂O₂ generation efficiency (208.75 mmol/dm³ after 60 min). This result is approximately four times higher than pure ZnO (50.47 mmol) and the IMP sample (62.18 mmol). A_IMP_H (62.19 mmol), ADS_E (57.04 mmol) and A_IMP (21.24 mmol) samples showed moderate to low H₂O₂ production.

The enhanced H₂O₂ generation in IMP_H suggests that hydrothermal impregnation facilitates more efficient electron transfer to molecular oxygen, which promotes two-electron reduction pathway (Eq. 9). The increased temperature and pressure are likely to improve the interfacial contact between CDs and ZnO, creating more effective active sites for oxygen reduction. In contrast the A_IMP samples show the lowest H₂O₂ generation efficient, suggesting that APTES functionalization may change the electronic structure or surface charge, redirecting electrons toward other reactive oxygen species rather than H₂O₂ accumulation.

Superoxide radical generation under Xe lamp irradiation was different from the generation of •OH radicals and H₂O₂ (Fig. 9b). IMP and IMP_H composites showed the highest O₂^{•-} production, indicating that these impregnation methods promote electron transfer to molecular oxygen, generating superoxide radicals. This is consistent with the high H₂O₂ generation efficiency of IMP_H, as O₂^{•-} is a precursor to H₂O₂ (Eq. 10).

APTES – modified materials showed moderate O₂^{•-} generation efficiency. This suggests that APTES may influence interfacial charge transfer and redistribute photogenerated electrons among competing reduction pathways, rather than maximizing superoxide formation alone. The relatively low O₂^{•-} production efficiency by ADS_E further indicates that the efficiency of ROS generation depends not only on the amount of superoxide produced, but also on the balance between electron transfer, surface properties, and the subsequent conversion of reactive intermediates.

Under UV-Vis irradiation, the $\bullet\text{OH}$ generation results (Fig. 9c) A_IMP showed the highest efficiency (329.78 nM after 30 min), followed by A_IMP_H (311.77 nM), IMP (198.02 nM), IMP_H (177.61 nM), ZnO (177.06 nM) and ADS_E (154.97 nM).

The unmodified ZnO and IMP_H samples showed relatively low $\bullet\text{OH}$ radical generation under the Xe lamp, suggesting that full-spectrum UV-Vis light is less effective for the wide band gap of pure ZnO. However, the fact that A_IMP and A_IMP_H still show high efficiency under UV-Vis irradiation proves that CDs extend photoactivity into the visible region, enabling the production of $\bullet\text{OH}$ radicals in a broader radiation spectrum.

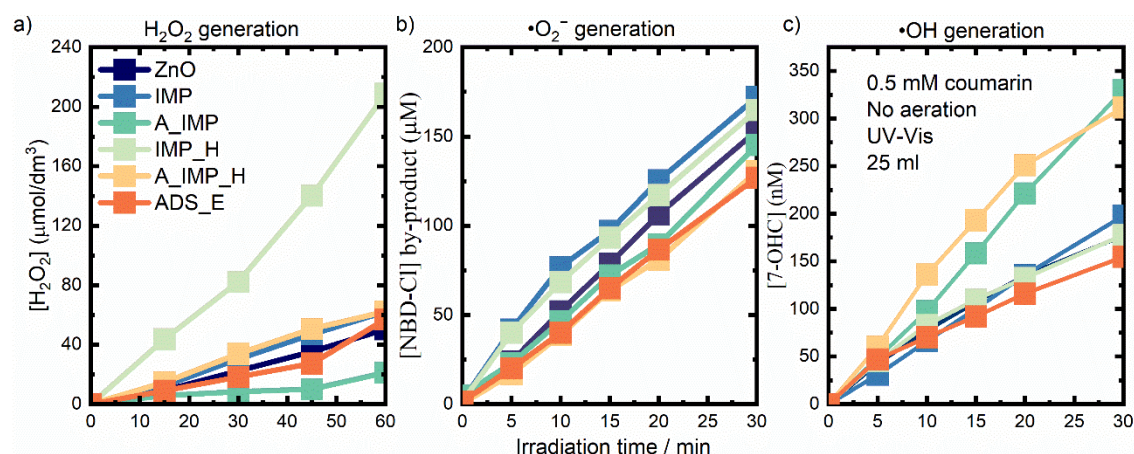


Figure 9. Efficiency of ROS generation for pure ZnO and CDs@ZnO hybrid materials under UV-Vis irradiation a) H_2O_2 production, b) $\text{O}_2^{\bullet-}$ generation c) $\bullet\text{OH}$ generation.

Naproxen degradation

The photocatalytic degradation of NPX was highly dependent on the irradiation range and catalyst structure (Fig. 10). Under visible light irradiation, the photocatalytic efficiency was clearly differentiated between the samples, with A_IMP and A_IMP_H showing the highest activity, followed by ADS_E, while ZnO and IMP were less effective. In contrast, under UV-Vis irradiation, all materials showed high degradation efficiency.

Photolysis studied under Xe lamp also revealed a decrease in NPX concentration, confirming that degradation under these conditions is a major contributor. In visible light, photolysis was low, confirming that this degradation originates primarily from the photocatalysts rather than from direct irradiation of NPX. These results demonstrate that CDs@ZnO hybrid materials are especially important under visible light conditions, where unmodified ZnO shows limited activity, while under UV-Vis irradiation, the contribution of direct photolysis partially masks the differences between the samples. To clearly confirm whether the decrease in NPX concentration observed in the photocatalytic tests

resulted from its actual decomposition into simple inorganic compounds (CO_2 and H_2O) or only from partial transformation into other, potentially toxic organic intermediates, the degree of total organic carbon (TOC) reduction was determined after the UV-Vis light irradiation process. The results obtained are summarised in Table 8.

The analysis showed that pure ZnO exhibited the highest TOC reduction capacity. The introduction of CDs into the hybrid materials reduced this parameter, which can be attributed to several factors related to interfacial engineering strategies. Under photocatalytic conditions, CDs bound to the surface or the organic linker (APTES) can undergo oxidation and degradation by the photogenerated ROS. This competitive consumption of ROS impairs the system's ability to achieve full mineralization.

Among the hybrid materials, the IMP sample achieved the highest TOC reduction, followed by IMP_H and A_IMP_H. The lowest mineralization efficiencies were observed for the A_IMP and ADS_E samples. In the case of ADS_E, the sample's morphology may promote specific redox pathways while simultaneously blocking active catalytic sites that are necessary for the deep oxidation of degradation intermediates to CO_2 and H_2O .

The use of hydrothermal treatment for the silanized sample (A_IMP_H) increased TOC reduction efficiency compared to the silanized sample using simple impregnation (A_IMP). According to the BET analysis, this enhancement cannot be attributed to aggregate disruption and the exposure of additional active sites, as was the case for the IMP_H sample. However, the application of hydrothermal conditions to the APTES shell likely led to the formation of rigid, covalent interfacial bonds, thereby improving the efficiency of interfacial charge transfer. This allows for more efficient catalytic activity and a more effective decomposition of intermediates into CO_2 and H_2O .

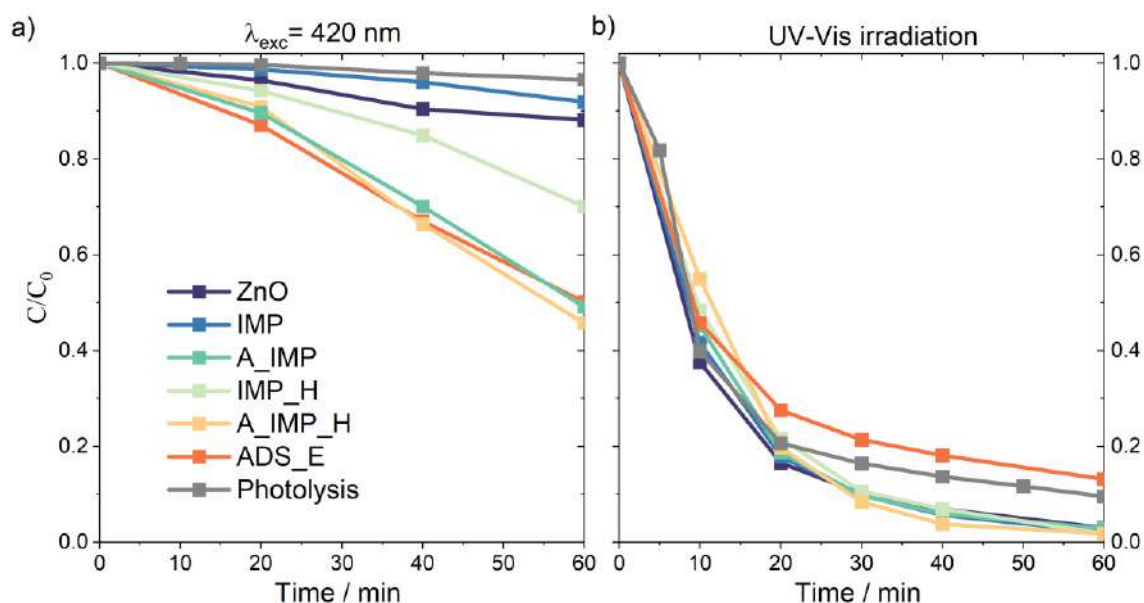


Figure 10. Efficiency of naproxen degradation for pure ZnO and hybrid materials under a) 420 nm irradiation and b) UV-Vis irradiation.

Table 8. Photocatalytic activity of pure ZnO and CDs@ZnO hybrid materials.

Sample	NPX degradation efficiency in Vis, %	NPX degradation efficiency in UV-Vis, %	Efficiency of TOC reduction, %
ZnO	11.83	96.97	34.03
IMP	8.07	97.86	26.05
A_IMP	49.86	86.79	6.45
IMP_H	54.23	98.19	19.07
A_IMP_H	50.84	97.12	18.37
ADS_E	29.91	98.22	1.59

The complete set of results indicates that the observed reactivity arises from a combination of light absorption, charge separation, reactive oxygen species formation, and surface interactions. The H_2O_2 measurements show that electron transfer to oxygen occurs effectively, especially in hydrothermally prepared samples. $\bullet\text{OH}$ radical generation experiments demonstrate that hydroxyl radicals are strongly produced under both 375 nm and UV-Vis irradiation, with the APTES-modified samples showing the most favorable response. $\text{O}_2^{\bullet-}$ radical generation results confirm that these radicals are also formed, although their efficiency does not directly reflect the final degradation yield. This

indicates that superoxide radicals are an intermediate species rather than the only active oxidant.

Taken together with the NPX degradation and photolysis, the results support a mechanism in which CDs@ZnO composites absorb light, generate electron-hole pairs, reduce oxygen to $O_2^{\bullet-}$ convert part of it into H_2O_2 , and further produce $\bullet OH$, while holes can also contribute directly to oxidation. APTES functionalization appears to improve the overall process by modifying the surface environment and enhancing pollutant-catalyst interaction, whereas CDs extend the photoresponse toward the visible range and suppress charge recombination. This indicates that the material exhibiting the best properties does not rely on a single dominant reactive species but rather on the synergistic effects of generated ROS, interfacial charge transfer, and favorable surface chemistry.

4. Conclusions

In summary, this work demonstrates that the precise selection of the surface engineering strategy used to deposit CDs on ZnO is a key factor determining not only the textural and optical properties of the resulting CDs@ZnO hybrid materials but, above all, their selective photocatalytic activity in oxidation or reduction processes under the influence of UV-Vis light. XRD structural studies confirmed the preservation of the pure wurtzite phase in all impregnation methods. However, systematic shifts of the diffraction reflections toward higher 2θ angles revealed the presence of variable compressive stresses and crystalline contraction which were induced by the involvement of ZnO surface oxygen in forming strong interfacial bonds with CDs during the impregnation process.

The material obtained by the simple impregnation method exhibited the lowest CDs incorporation efficiency, with the dots only weakly bonded to the surface of the ZnO aggregates. This loose packing partially blocked the oxide pores, decreasing the S_{BET} surface area and pore volume. Optically, the lack of strong electronic coupling between the phases caused the dots to behave as isolated centers, as evidenced by the maintenance of a high UV-to-visible excitation ratio. In terms of photoluminescence, the IMP sample exhibited increased emission intensity in the visible region, indicating that the CDs functioned primarily as independent emission centers rather than as effective charge acceptors. This resulted in a high capacity to generate $O_2^{\bullet-}$ radicals but limited efficiency in NPX oxidation or H_2O_2 production. The introduction of the molecular silane linker APTES prior to impregnation of the A_IMP sample enabled the formation of a layer that

strengthened the CDs-ZnO bond. The presence of APTES limited accessibility to the oxide pores, resulting in an intermediate S_{BET} value. At the same time, this material demonstrated the highest excitation efficiency in the visible range. This proves that the binding preserves the original electronic states and unique optical properties of CDs. Under UV-Vis light, the A_IMP sample achieved the highest efficiency of hydroxyl radical generation, demonstrating that CDs effectively enhance photoactivity in the visible range and open alternative water oxidation pathways, despite simultaneously showing the lowest efficiency in the hydrogen peroxide accumulation process.

A completely different structural and morphological reorganization was observed for the IMP_H sample obtained by hydrothermal impregnation. Elevated pressure and temperature induced the disruption of ZnO aggregates, resulting in a more than twofold increase in specific surface area, the highest value in the entire series, along with a simultaneous increase in pore volume. This was accompanied by the largest shrinkage of the unit cell volume, indicating strong integration of CDs within the ZnO layer. In photocatalytic tests, the IMP_H material proved to be a highly optimized, reduction-driven photocatalyst, demonstrating a fourfold increase in H_2O_2 generation efficiency and high production of $\text{O}_2^{\bullet-}$ radicals, confirming the formation of specific active sites that favor the two-electron oxygen reduction pathway. The A_IMP_H sample represents the most advanced engineering architecture, combining APTES pre-modification with hydrothermal treatment. The silane layer formed a stable Si-O-Zn bond that mechanically bound the ZnO grains and created a protective coating, resulting in S_{BET} and unit cell volumes comparable to those of pure ZnO. TEM studies confirmed the formation of a continuous hybrid layer several nanometers thick and densely saturated with CDs. This structure induced quenching of the ZnO defect luminescence. The shortened emission lifetime at 440 nm confirmed the opening of effective nonradiative charge-relaxation channels directly from the ZnO conduction band. In turn, the significant extension of the emission lifetime in the visible region demonstrates the formation of stable, long-lived interfacial trap states. These states effectively retard radiative recombination of charge carriers, extending the availability of photogenerated holes. As a result, the A_IMP_H material proved to be an effective oxidation photocatalyst, demonstrating the highest $\bullet\text{OH}$ radical production under monochromatic 375 nm irradiation and high NPX photodegradation efficiency under visible light.

The final material, ADS_E, revealed unique surface morphology. Precise pH control allowed the exploitation of Coulomb forces between the positive surface potential of ZnO and the negatively charged outer shell of CDs. This enabled uniform, dense packing and a well-defined spatial orientation of CDs. This interaction induced the selective growth of local, elongated crystalline protrusions on ZnO, increasing S_{BET} and inducing contraction of the crystal lattice. These changes led to the dominance of a single UV excitation band due to the restructuring of electronic states near the band gap. Although the ADS_E sample exhibited a prolonged luminescence lifetime due to the formation of stable interfacial trap states, its specific configuration limited the kinetics of free-radical generation in solution. Despite its lower efficiency in ROS results, this material demonstrated high activity in the photodegradation of NPX under visible light. This demonstrates that the long lifetime of photoinduced charge carriers and the forced interfacial structure of ADS_E promote strong adsorption of the organic pollutant, thereby directing the photocatalytic process toward an efficient pathway of direct substrate oxidation via long-lived holes, bypassing traditional free radical intermediates.

In summary, the conducted studies clearly demonstrate that the composition and interfacial chemistry of CDs@ZnO heterostructures can be precisely tuned to direct photogenerated charge carriers toward desired redox pathways. While mechanical and chemical capping of the coating via silanization combined with hydrothermal treatment (A_IMP_H) optimizes the interfaces for the visible oxidation of organic pollutants, high-pressure hydrothermal impregnation without linkers (IMP_H) remodels the textural framework to favor green hydrogen peroxide synthesis via reduction. These relationships provide a universal design platform for the creation of high-performance, selective hybrid photocatalysts for targeted environmental and energy applications

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9. Summary

The conducted studies clearly demonstrated that CDs are a class of nanomaterials whose optical properties can be broadly modified by the appropriate selection of synthesis conditions, chemical composition, and surface structure. The results confirmed that the emission of these materials is a complex phenomenon arising from the coexistence of multiple photophysical processes, including emission associated with surface states, charge transfer, and interactions between the core and surface functional groups. Consequently, CDs should be considered highly complex systems but also as materials susceptible to modification, making them interesting for the further development of luminescent materials.

A particularly important conclusion from the conducted studies is that synthesis plays a key role in determining the emission mechanism and luminescence efficiency of CDs. The presence of acidic modifiers was shown to promote the stabilization of surface trapping states, leading to extended fluorescence lifetimes. In turn, alkaline or aprotic conditions enable more efficient charge transfer processes, resulting in significant reductions in energy losses and very high quantum yields. This means that by consciously shaping the synthesis, one can not only influence the emission intensity but also control the dominant mechanism responsible for the material's optical properties. This is important for the further development of CDs as functional materials for applications in optoelectronics, diagnostics, and sensor technology.

An equally important result was the indication that CDs exhibit high sensitivity to environmental changes. In the case of the CDs used in one study, they exhibited high sensitivity to pH changes and to the presence of hydroxyl groups in organic solvents. The resulting materials exhibited a wide range of optical responses, confirming their suitability as molecular sensors. The results of spectroscopic analyses showed that the mechanism of their response is not solely due to analyte-fluorophore interactions but rather reflects complex processes occurring at the interface. These include protonation/deprotonation of surface groups, the formation and breaking of hydrogen bonds, and local changes in the structural organization of nanoparticle surfaces. This behavior allows CDs to serve as a basis for the design of modern, biocompatible fluorescent sensors with high sensitivity and simple, inexpensive fabrication.

An important part of the dissertation also concerned the use of CDs as components of hybrid systems for heterogeneous photocatalysis. Incorporating CDs into TiO₂ systems improved photocatalytic activity in the UV range and enabled use of visible light, an advantage for practical environmental applications. The results confirmed that CDs play several roles in such systems: they broaden the system's absorption range, facilitate charge carrier separation, limit recombination, and increase the efficiency of processes that lead to ROS formation. This multifunctionality makes them a valuable component of modern photocatalysts, particularly for degrading persistent organic pollutants in aquatic environments.

More detailed conclusions can be drawn from studies of CDs@ZnO hybrid systems, which have demonstrated that the method used to combine the two phases is crucial to their final catalytic properties. The use of various interface modification strategies enabled control over photocatalytic processes and demonstrated that the heterojunction architecture determines whether oxidation or reduction reactions dominate the system. In particular, it was demonstrated that a well designed interface can enhance charge transfer between the hybrid components, thereby increasing the degradation efficiency of compounds such as NPX. At the same time, it was noted that excessive organic phase content can lead to competing autodegradation processes and ROS consumption, limiting the system's efficiency. Consequently, enhancing system efficiency relies not only on combining CDs with the semiconductor but, more importantly, on the precise architectural design and configuration of their interface

In summary, the obtained results confirm that CDs are materials with exceptionally high application potential, the full utilization of which requires a precise understanding of the relationships between their chemical structure, optical properties, and behavior in material systems. The research conducted expands our understanding of luminescence mechanisms in carbon nanostructures and provides new insights into their roles in sensing and photocatalytic systems. It demonstrates that, through appropriate surface modification and interface engineering, systems with desired functional properties can be designed, opening prospects for further development of materials for environmental remediation, analyte detection, and other advanced chemical technology applications.

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Copies of co-authors' statements



Wrocław, 11.06.26 r.

mgr inż. Daniela Kujawa
Oddział Spektroskopii Optycznej

Oświadczenie o wkładzie mgr inż. Danieli Kujawa w publikacje wchodzące w skład cyklu prac

I confirm my participation in the following publications

P1. D.Kujawa, R. Tomala, P. Gluchowski, *Tailoring Emission Mechanisms in Carbon Dots through Controlled Surface Chemistry*, Applied Surface Science, 2026, 736, 10.1016/j.apsusc.2026.166772, (IF = 6.9, MNiSW Points: 140)

P2. D.Kujawa, M. Ptak, P. Gluchowski, *A Rapid, Green and Cost-Effective Synthesis of pH- and Hydroxyl Group Sensitive Carbon Dots for Sensing Applications*, Journal of Materials Chemistry C, 2025, 13, 32, 16364-72, 10.1039/D5TC02262B, (IF = 5.2, MNiSW Points: 140)

P3. D. Kujawa, A. Grzegorska, A. Zielinska-Jurek, M. Fandzloch, O. Bezkravnyi, P. Gluchowski, *Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst*, Dalton Transactions, 2025, 54(4), 1504-1520, 10.1039/D4DT02196G, (IF = 3.3, MNiSW Points: 140)

P4. D. Kujawa, M. Kowalkińska, O. Bezkravnyi, A. Zielińska-Jurek, P. Gluchowski, *CDs@ZnO Photocatalysts with Interfacial-Dependent Oxidative and Reductive Activity*, - manuscript ready for submission

In the mentioned works, my contribution consisted of:

- **P1:** Conceptualization, planning material modifications, synthesis of CDs samples with different modifiers, conducting synthesis, preparing materials for measurements, performing spectroscopic measurements, analyzing the results of spectroscopic and structural measurements, data processing and preparing their graphic visualization, planning the structure of the manuscript, describing the results, preparing the initial and final versions of the manuscript, preparing responses to reviewers, archiving data after preparing the final article
- **P2:** conceptualization, carrying out chemical synthesis, selecting reagents and performing preliminary tests of their effect on the optical properties of materials, preparing materials for structural and morphological studies, performing spectroscopic measurements, analyzing the results of spectroscopic, XRD and TEM measurements and preliminary analysis of IR results, data processing and preparing their graphic visualization, planning the structure of the manuscript, preparing the initial and final versions of the manuscript, preparing responses to reviewers, archiving data after preparing the final article;

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- **P3:** conceptualization, synthesizing CDs, preparing hybrid materials, preparing materials for structural and morphological studies, performing spectroscopic measurements, processing data and preparing their graphic visualization, analyzing the results, planning the structure of the manuscript, proposing the energy transfer mechanism, preparing the initial and final versions of the manuscript, preparing responses to reviewers, archiving data after preparing the final article;
- **P4:** conceptualization, planning material impregnation methods, conducting chemical synthesis, preparing hybrid materials, preparing materials for structural and morphological studies, conducting spectroscopic measurements, data processing and preparing their graphic visualization, analyzing the results, planning the manuscript structure, proposing the energy transfer mechanism, preparing the initial and final versions of the manuscript, archiving data after preparation of the final article;

Lujawa Dawid

dr hab. Paweł Głuchowski

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Declaration of the co-authorship of the publications

I confirm my participation in the following publications:

- D.Kujawa, R. Tomala, **P. Głuchowski**, *Tailoring Emission Mechanisms in Carbon Dots through Controlled Surface Chemistry*, Applied Surface Science, 2026, 736, 10.1016/j.apsusc.2026.166772
- D. Kujawa, A. Grzegorska, A. Zielinska-Jurek, M. Fandzloch, O. Bezkravnyi, **P. Głuchowski**, *Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst*, Dalton Transactions, 2025, 54(4), 1504-1520, 10.1039/D4DT02196G
- D.Kujawa, M. Ptak, **P. Głuchowski**, *A Rapid, Green and Cost-Effective Synthesis of pH- and Hydroxyl Group Sensitive Carbon Dots for Sensing Applications*, Journal of Materials Chemistry C, 2025, 13, 32, 16364-72, 10.1039/D5TC02262B
- D. Kujawa, M. Kowalkińska, O. Bezkravnyi, A. Zielińska-Jurek, **P. Głuchowski**, *CDs@ZnO Photocatalysts with Interfacial-Dependent Oxidative and Reductive Activity*, Manuscript ready for submission

As the supervisor of M. Sc. Eng. Daniela Kujawa, I was responsible for supervising, reviewing, and editing manuscripts.

I confirm that M. Sc. Eng. Daniela Kujawa was the lead co-author in mentioned publications.

dr hab. Paweł Głuchowski


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dr hab. Maciej Ptak

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Declaration of the co-authorship of the publication

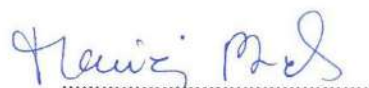
I confirm my participation in the following publications:

- D.Kujawa, **M. Ptak**, P. Gluchowski, *A Rapid, Green and Cost-Effective Synthesis of pH- and Hydroxyl Group Sensitive Carbon Dots for Sensing Applications*, Journal of Materials Chemistry C, 2025, 13, 32, 16364-72, 10.1039/D5TC02262B

My contribution to this publication involved the interpretation of the IR spectra and data analysis.

I confirm that M. Sc. Eng. Daniela Kujawa was the lead co-author in mentioned publication.

dr hab. Maciej Ptak



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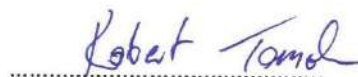
I confirm my participation in the following publications:

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My contribution to this publication involved project supervision and reviewing the manuscript.

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- D. Kujawa, A. Grzegorska, A. Zielinska-Jurek, **M. Fandzloch**, O. Bezkravnyi, P. Gluchowski, *Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst*, Dalton Transactions, 2025, 54(4), 1504-1520, 10.1039/D4DT02196G

My contribution to this publication involved the synthesis of titanium dioxide and BET characterization.

I confirm that M. Sc. Eng. Daniela Kujawa was the lead co-author in mentioned publication.

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- D. Kujawa, A. Grzegorska, A. Zielinska-Jurek, M. Fandzloch, **O. Bezkravnyi**, P. Gluchowski, *Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst*, Dalton Transactions, 2025, 54(4), 1504-1520, 10.1039/D4DT02196G
- D. Kujawa, M. Kowalkińska, **O. Bezkravnyi**, A. Zielińska-Jurek, P. Głuchowski, *CDs@ZnO Photocatalysts with Interfacial-Dependent Oxidative and Reductive Activity*, Manuscript ready for submission

My contribution to this publication consisted of TEM imaging.

I confirm that M. Sc. Eng. Daniela Kujawa was the lead co-author in mentioned publications.

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- D. Kujawa, A. Grzegorska, A. Zielinska-Jurek, M. Fandzloch, O. Bezkravnyi, P. Gluchowski, *Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst*, Dalton Transactions, 2025, 54(4), 1504-1520, 10.1039/D4DT02196G

My contribution to this publication consisted of conducting photocatalytic activity measurements and data analysis.

I confirm that M. Sc. Eng. Daniela Kujawa was the lead co-author in mentioned publications.

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- D. Kujawa, **M. Kowalkińska**, O. Bezkravnyi, A. Zielińska-Jurek, P. Gluchowski,
*CDs@ZnO Photocatalysts with Interfacial-Dependent Oxidative and Reductive
Activity*, Manuscript ready for submission

My contribution to this publication consisted of conducting photocatalytic activity measurements and reviewing the manuscript.

I confirm that MSc. Eng. Daniela Kujawa was the lead co-author in mentioned publications.

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- D. Kujawa, A. Grzegorska, A. Zielińska-Jurek, M. Fandzloch, O. Bezkravnyi, P. Gluchowski, *Enhancement of carbamazepine photodegradation using hybrid of phosphorescent carbon dots coupled with highly porous TiO₂ photocatalyst*, Dalton Transactions, 2025, 54(4), 1504-1520, 10.1039/D4DT02196G
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My contribution to this publication was analysis of photocatalytic activity data and reviewing manuscripts.

I confirm that M. Sc. Eng. Daniela Kujawa was the lead co-author in mentioned publications.

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